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Contents of Vol. XXXVII.

No. 1.

CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF THE NEBRASKA WESLEYAN UNIVERSITY:
XIII.—*Studies on the Soils of the Northern Portion of The Great Plains Region: The Third Steppe.* By Frederick J. Alway and Ross A. Gortner 1
CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF HARVARD COLLEGE:
On Certain Derivatives of Tetrachlororthobenzoquinone. By C. Loring Jackson and R. D. MacLaurin . . . 7
CONTRIBUTION FROM THE KENT CHEMICAL LABORATORY OF THE UNIVERSITY OF CHICAGO:
On Aldol, Pentaerythrose and the Action of Copper Acetate on the Hexoses. By A. F. McLeod 20
ACYL DERIVATIVES OF ORTHO- AND PARAMINOPHENOL. By J. Bishop Tingle and L. F. Williams 51
ON THE SALTS OF TAUTOMERIC COMPOUNDS. By S. F. Acree . . 71
CONTRIBUTION FROM THE TEXAS EXPERIMENT STATION:
A Simple Fat Extraction Apparatus. By G. S. Fraps . . 85
CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF HARVARD COLLEGE:
On the Constitution of the α- and β-Addition Compounds of Alcohols and Tetrabromorthobenzoquinone. By C. Loring Jackson and R. D. MacLaurin 87

NOTE.

Dry Method for the Generation of Oxygen from Sodium Peroxide . 106

REPORTS.

Thiophosphoric Acids and Thiophosphates 107
On a Method for Determining the Specific Heat of Solutions; Contribution to the Study of Hydrates 112

REVIEWS.

Analyse des métaux par Électrolyse 114
Premier Congres International pour L'Etude de la Radiologie et de L'Ionisation 115
The Elements of Chemical Engineering 116
Sechs Vorträge über das Thermodynamische Potential . . . 117
General Principles of Organic Syntheses 117

No. 2.

CONTRIBUTIONS FROM THE SHEFFIELD LABORATORY OF YALE UNIVERSITY:
  - *The Double Ammonium Lead Chlorides.* By H. W. Foote and L. H. Levy 119
  - *The Double Caesium Lead Bromides.* By H. W. Foote . 124

THE ABSORPTION SPECTRA OF CERTAIN SALTS IN AQUEOUS SOLUTION AS AFFECTED BY THE PRESENCE OF CERTAIN OTHER SALTS WITH LARGE HYDRATING POWER. By Harry C. Jones and Horace S. Uhler 126

REPORT.

The Mechanism of Carbon Assimilation in Green Plants . . . 196

REVIEWS.

Amerikanisches Hochschulwesen 198
Researches on Cellulose 199
The Principles of Qualitative Analysis, from the Standpoint of the Theory of Electrolytic Dissociation and the Law of Mass Action 201
Lecture-Notes on Chemistry for Dental Students 202
Portland Cement 203
Monographien über angewandte Elektrochemie 204
A Text-Book of Sanitary and Applied Chemistry of the Chemistry of Water, Air and Food 205
Cours de Chimie Organique 206

No. 3.

THE ABSORPTION SPECTRA OF CERTAIN SALTS IN AQUEOUS SOLUTION AS AFFECTED BY THE PRESENCE OF CERTAIN OTHER SALTS WITH LARGE HYDRATING POWER. By Harry C. Jones and Horace S. Uhler (*Continued*) 207
THE ABSORPTION SPECTRA OF CERTAIN SALTS IN NON-AQUEOUS SOLVENTS, AS AFFECTED BY THE ADDITION OF WATER. By Harry C. Jones and Horace S. Uhler 244
CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF THE NEBRASKA WESLEYAN UNIVERSITY:
  - XIV.—*Studies on the Soils from the Northern Portion of The Great Plains Region: The Distribution of Carbonates on the Second Steppe.* By Frederick J. Alway and Guy R. McDole 275

OBITUARY.

Dmitri Ivanowitsh Mendeléeff 283

REPORT.

Oxides of the Alkali Metals 285

NOTE.

The Generation of Oxygen from Sodium Peroxide 286

REVIEWS.

Chemical Abstracts 287
La Grande Industrie Chimique 288
Anleitung zur vereinfachten Elementaranalyse 289
Vorlesungen über Anorganische Chemie für Studierende der Medizin 290
Jahrbuch der Chemie 291
Der Nachweis von Schriftfälschungen, Blut, Sperma, u. s. w. . . 291
An Elementary Study of Chemistry 292

No. 4.

CONTRIBUTION FROM THE KENT CHEMICAL LABORATORY OF THE UNIVERSITY OF CHICAGO:
On the Behavior of Sodium and Sodium Alcoholates towards Various Esters of Acetic Acid. By Louis Allen Higley. 293
THE OSMOTIC PRESSURE AND THE DEPRESSION OF THE FREEZING POINTS OF SOLUTIONS OF GLUCOSE. By H. N. Morse, J. C. W. Frazer and B. F. Lovelace 324
ON SOME SEMICARBAZIDE DERIVATIVES OF ISOPROPIONIC ACID, BENZOIC ACID AND BENZENESULPHONIC ACID. By S. F. Acree. 361
THE REACTION BETWEEN UNSATURATED COMPOUNDS AND ORGANIC MAGNESIUM COMPOUNDS. By E. P. Kohler 369
CONTRIBUTION FROM THE SHEFFIELD LABORATORY OF YALE UNIVERSITY:
CXLII.—*Researches on Pyrimidines: Synthesis of Uracil-5-Carboxylic Acid.* By Henry L. Wheeler, Treat B. Johnson and Carl O. Johns 392
A POSSIBLE EXPLANATION OF THE INCREASE IN VISCOSITY WHICH RESULTS WHEN THE ALCOHOLS ARE MIXED WITH WATER; AND OF THE NEGATIVE VISCOSITY COEFFICIENTS OF CERTAIN SALTS WHEN DISSOLVED IN WATER. By Harry C. Jones and W. R. Veazey 405
STUDIES IN CATALYSIS: THE REARRANGEMENT OF ACETYLHALOGENAMINOBENZENE DERIVATIVES INTO HALOGEN ACETANILIDE DERIVATIVES. By S. F. Acree and J. M. Johnson . . . 410

OBITUARY.

Nicolai Alexandrowitsch Menschutkin 413
Henri Moissan 413
Hendrik Willem Bakhuis-Roozeboom 415

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Vol. XXXVII. January, 1907. No. 1.

AMERICAN

CHEMICAL JOURNAL

Contributions from the Chemical Laboratory of the Nebraska Wesleyan University.

XIII. STUDIES ON THE SOILS OF THE NORTHERN PORTION OF THE GREAT PLAINS REGION: THE THIRD STEPPE.

By Frederick J. Alway and Ross A. Gortner.

The third steppe extends from the Missouri Coteau westward to the Rocky Mountains or the bordering foot-hills, including the portions of Alberta and western Saskatchewan south of the North Saskatchewan River. The altitude varies from about 2100 feet on the east to over 4,000 feet at the foot of the mountains. The greater part of the steppe is almost entirely devoid of forest. Cacti and other xerophytic plants attest to the arid character of the southern portion. Numerous alkali lakes without outlets serve as evaporating basins for a large part of the run-off. The analysis of water from the largest of these, Old Wives Lake, is given below. Its chief constituent is sodium sulphate. The mean winter temperature on this steppe rises steadily in passing from east to west. The proportion of bright sunshine is high; in connection with this it is interesting to note the deep violet color acquired by

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colorless glass that has been exposed, for some time, upon this steppe, to the sunshine. The nature of the soil is too varied to admit of generalizations. There are considerable areas of bare drifting sand-hills and tracts of barren, stiff clay of the typical Bad Lands character, as well as the more extensive, fertile, grass-covered plains. In general, the soil is more sandy and gravelly than that of the second steppe. The soils analyzed were taken from the wide, grassy plain at the western border. The surface soils are rich in nitrogen, potash and lime and are well provided with phosphoric acid. The subsoil differs in mineral constituents from the preceding chiefly in the much larger amount of calcium and magnesium carbonates and in a somewhat smaller amount of potash. Both contain considerable quantities of water-soluble salts, which in many places over the area have been partly leached out into the depressions, forming tracts of alkali-lands. The composition of the samples agrees with the generalizations made by Hilgard[1] in regard to the relations of soils to climate. The rather large proportion of manganese in the subsoil doubtless bears no relation to the change in the color of the glass lying on the surface.

Analysis of Water from Old Wives Lake.

This lake, which is 2,165 feet above sea-level and lies near the eastern edge of the steppe, serves as an evaporating basin for the drainage of a region about 5,000 square miles in area. Its composition will, accordingly, indicate the nature of the water-soluble salts occurring in the soil over a considerable part of the steppe. The lake is divided into two parts, a southern, called Lake Johnston, and a northern, Lake Chaplin. The two are connected by a channel 10 miles in length, which serves to keep the surface of the two divisions at the same level. All the creeks, which feed the lake, unite to form Old Wives Creek, which empties into the channel near its southern end. Differences in the composition of the water of the two portions of the lake are likely to be confined to the concentration of dissolved salts and not to extend to the relative proportions of these.

[1] Wollny's "Forschungen," 16, 51–91.

The sample of water used in this analysis was collected by one of the writers, near the northern shore of Lake Chaplin and near the railway station of the same name, in July, 1904. At the time of collection the water emitted a distinct odor of hydrogen sulphide and carried only traces of suspended matter. The sample was so small that some of the constituents were not determined.

The sp. gr. of the water at 15° was 1.018. The weight of solids, dried at 180°, was 27.7055 grams per liter.

Analysis:

	Grams per liter.	Total inorganic material in solution. Per cent.
Sodium (Na)	8.3674	30.20
Potassium (K)	trace	. .
Calcium (Ca)	"	. .
Magnesium (Mg)	0.2677	0.96
Aluminium (Al)	trace	.
Chlorine (Cl)	1.3623	4.91
Carbonate (CO_3)	0.4200	1.52
Sulphate (SO_4)	16.8883	60.96
Silicate (SiO_3)	trace	. .
Total	27.3057	98.55

Analysis of Surface Soil and Subsoil.

The samples analyzed were taken by one of the writers in April, 1906, from near Gleichen. The surface soil, to a depth of 12 inches, was secured from several different places and thoroughly mixed for sample No. 1. No. 2 was prepared by mixing 100 gram portions of each foot section, from the second to the sixth, obtained from 2 borings. The method of analysis employed was that of Hilgard.[1] A weighed quantity of fine material, below 0.5 mm. in diameter, which had been dried at 100°, was placed in a porcelain beaker, covered with a watch glass, treated with from 8–10 times its bulk of hydrochloric acid, sp. gr. 1.115, and a few drops of nitric acid, and digested for 5 days over a steam bath.

[1] Cal. Agr. Expr. Station, Circular 6 (1903).

	No. 1. Surface soil.		No. 2. Subsoil.	
Insoluble matter	62.85	77.99	60.67	73.02
Soluble silica	15.14		12.35	
Potash (K_2O)		1.29		0.84
Soda (Na_2O)		0.33		0.29
Lime (CaO)		1.03		6.43
Magnesia (MgO)		0.71		1.70
Brown oxide of manganese (Mn_3O_4)		0.07		0.22
Peroxide of iron (Fe_2O_3)		4.61		3.31
Alumina (Al_2O_3)		5.17		4.50
Phosphoric acid (P_2O_5)		0.16		0.15
Sulphuric acid (SO_3)		0.67		0.12
Carbonic acid (CO_2)		0.39		5.68
Water and organic matter		7.75		3.60
Total		100.17		99.86
Nitrogen		0.22		. .
Hygroscopic coefficient at 10°		5.7		4.5

The soil was evidently of lacustral origin, being free of stones or gravel and being underlaid by boulder clay.

The Action of Sunshine upon Colorless Glass Exposed upon the Third Steppe.

After glass objects, that were originally colorless, have been exposed for some time to the direct sunshine upon this steppe, their appearance is quite remarkable. Apparently they all soon assume a more or less intense violet coloration. This color is in very many cases sufficiently intense to be easily recognizable from the windows of a moving train. Deeply colored glass bottles or broken pieces of glass were observed by one of the writers, at frequent intervals, all the way from Calgary, on the extreme western edge of the steppe, to the eastern border at the Missouri Coteau. A few less strongly colored specimens were found at Moose Jaw, on the second steppe. As the ground at the last-mentioned place was covered with snow at the time and thus obscured nearly all glass objects that had been exposed to the sunshine, it would not be justifiable to conclude that glass exposed on the western part of the second steppe will differ in the extent of the color change from that lying, under similar conditions, on the eastern part of the third steppe.

At the village of Gleichen, and at the city of Calgary there are large quantities of glass on the garbage grounds. These were examined in the hope of finding colorless glass that bore evidence of long exposure, or glass, originally of a faint greenish shade, that had acquired a violet tint. In no case was ordinary window glass, or a glass jar or bottle showing a greenish color on broken edges, found to have acquired any violet coloration. Window panes that had been exposed to the direct sunshine for many years, as well as large heaps of broken window glass upon the surface of which were violet colored glass objects, were examined with the result that only a single piece, part of a pressed window pane of colorless glass, which showed a bluish-green color on the broken edges, was observed, that seemed an exception. Several pieces of this pane were found, those on the top of the heap being quite violet, even on the broken edges, while those buried in the heap, and so protected by the overlying ordinary window glass, were free from any violet tint. On analysis it was found to contain a large amount of manganese. All the specimens of colorless glass found gave evidence of not having been long exposed or of having been protected from the direct rays of the sun by soil or rubbish. The articles were of the most varied description, lamps, lamp-chimneys, tableware, medicine, pickle and preserve bottles. That the time of exposure of many of the violet colored bottles had not been long was evident from the almost perfect condition of the gummed paper labels. Violet colored glass, lying on grass of last season's growth, was observed on the prairie so frequently, and so far removed from any accumulation of glass, that it was necessary to conclude that the coloration had taken place since the close of last summer, *i. e.*, within 8 or 9 months. In none of these instances, of evidently brief exposure, was the maximum coloration observed.

While it has long been known that glass, decolorized by means of manganese compounds, gradually acquires a violet shade on long exposure to the direct sunlight, it does not seem to have been recognized until recently that the coloration may become apparent within a few years. Crookes[1] called attention to the subject in a description of some violet colored specimens of glass found in Bolivia at a considerable altitude, over 13,000 feet, and in a region of much bright sunshine. Fischer[2] has shown that the cause of this violet coloration is due to the action of the ultraviolet rays and can be produced within 12 hours by exposure to the rays from a mercury lamp, in glass containing readily recognizable amounts of manganese, while no change takes place in glass practically free from manganese. Similarly colored glass, from New Mexico, was reported by Avery,[3] who found considerable quantities of manganese in the specimens. This writer found, further, that the intensity of the coloration was approximately proportional to the manganese content. Simpson[4] observed glass prisms in West Australia to show a violet coloration after an exposure of between 1 and 2 years. Ruger,[5] finding colored glass at Butte, Montana, suggested that the violet color might be connected with the presence of manganese compounds, which occur in large quantities in the vicinity. From no other region, however, has such a wealth of specimens been reported as is to be found on the second prairie steppe of Canada.

After a long and careful search we have found a considerable number of violet colored specimens within a few miles of this university. The color, however, is faint compared with that of many of the specimens from Gleichen and Calgary. The most interesting specimen found here is a colorless glass bottle, which on August 26, 1905, was thrown by one of the writers upon a pile of stones. On May 1, 1906, a large piece of the bottle, lying on the top of the pile and fully exposed to the sunshine, was found to be distinctly colored violet. The other pieces of the bottle had fallen among the stones and were less strongly colored, some, that had been protected, being quite colorless. A qualitative test showed the presence of a very large amount of manganese.

[1] Chem. News, **91**, 73 (1905).

[2] Ber. d. Chem. Ges., **38**, 946 (1905).

[3] J. Am. Chem. Soc., **27**, 909 (1905).

[4] Chem. News, **91**, 236 (1905).

[5] J. Am. Chem. Soc., **27**, 1206 (1905).

In view of the above, it seems safe to conclude that varieties of colorless glass containing appreciable quantities of manganese may assume a violet tint, after an exposure to the sunshine of less than a year, both near the northwestern limit and near the eastern border of the great plains, independent of the altitude and of the temperature. It is probable that similar specimens will be found over the whole of the great plains region, the coloration being most intense in those from the western portions.

UNIVERSITY PLACE,
NEBRASKA,
July, 1906.

Contributions from the Chemical Laboratory of Harvard College.

ON CERTAIN DERIVATIVES OF TETRACHLORORTHOBENZOQUINONE.[1]

BY C. LORING JACKSON AND R. D. MACLAURIN.

After much time had been devoted in this laboratory to the study of the reactions of tetrabromorthobenzoquinone,[2] it seemed of interest to determine whether the tetrachlororthobenzoquinone behaved in the same way; and in the present paper we describe the first part of our work on this subject.

We prepared tetrachlororthoquinone, discovered by Zincke,[3] by a method similar to that given by him, which yielded good results, if certain precautions were carefully observed. In this way it was obtained as a bright red substance, melting at 133° to a dark red liquid. Zincke and Küster[4] give its melting point as 129°–130°.

The tetrachlororthoquinone is converted by tetrachlorpyrocatechin into the hexachlororthoquinopyrocatechin ether, $C_6Cl_4O_2.C_6Cl_2O_2$, which differs from the corresponding hexabrom compound[5] in having a lighter red color, melting at 300°, whereas the brom compound does not melt within the range of the thermometer, and being more soluble in the organic solvents, although it is still a slightly soluble substance.

---

[1] The work described in this paper formed part of a thesis presented to the Faculty of Arts and Sciences of Harvard University, for the degree of Doctor of Philosophy, by Robert D. MacLaurin.

[2] THIS JOURNAL, **26**, 10; **30**, 518; **31**, 89; **34**, 422, 460; **35**, 154.

[3] Ber. d. chem. Ges., **20**, 1779 (1887).

[4] *Ibid.*, **21**, 2730 (1888).

[5] Jackson and Koch: THIS JOURNAL, **26**, 35 (1901).

By reduction with sodium amalgam and water the orthoquino ether is converted into the hexachlordihydroxypyrocatechin ether, $C_6Cl_4O_2.C_6Cl_2(OH)_2$, which resembles the hexabrom compound[1] in crystallizing from alcohol in white needles, from other solvents in brown crystals, and by showing a surprisingly slight solubility in aqueous sodic hydrate; but it has a melting point 290°, instead of remaining unfused at temperatures within the range of the thermometer, and is more soluble in the common solvents. During the reduction of the hexachlororthoquinopyrocatechin ether a small amount of it is decomposed into substituted pyrocatechins, so that in this respect it also resembles the hexabrom compound.

In both these cases, therefore, the chlor compound resembles the corresponding one containing bromine with only such slight differences as would be expected. The same is true of the action of tetrachlororthoquinone on aniline dissolved in alcohol, as this yielded 4 products, the melting points of which are compared with those of the corresponding brom compounds in the following table:

	Cl.	Br.
$C_6X_2(C_6H_5NH)_2O_2$	194°–195°	160°
$C_6X_2(C_6H_5NH)_2O_2.C_6H_5NH_2$	164°–165°	121°–124°
$C_6X_2(C_6H_5NH)_2O_2.C_2H_5OH$	140°–141°	142°
$C_6HX(C_6H_5NH)_2ONC_6H_5$	180°	173°

That the last 2 compounds belong to the para series is shown by the fact that sulphurous dioxide, in ethereal solution, converts them into dianilinoparaquinoneanil,

$$C_6H_2(C_6H_5NH)_2ONC_6H_5,$$

as such a mild reaction carried on in the cold could not have brought about the change from the ortho to the para series. This inference is confirmed by the observations that the substance melting at 180° gives no addition compounds, and that sulphuric acid forms a purple solution with it, whereas it gives a green color with all the dianilinoorthoquinones studied. Conversions of ortho into paraquinones are far from uncommon.

---

[1] Jackson and Koch: *Ibid.*, **26**, 39 (1901). Jackson and Porter: *Ibid.*, **30**, 523 (1903).

The dianilinoparaquinoneanil was also formed by boiling any of the chlor compounds mentioned in the table with aniline and alcohol for 3–4 days, but this reaction is of no value in determining the constitution of these bodies, as the change from the ortho to the para series might well have taken place during this long process. As in previous work in this laboratory, great difficulty was experienced in raising the melting point of the dianilinoparaquinoneanil to 202°–203°. We therefore contented ourselves with proving the identity of our product by comparison with known samples of that body.

The behavior of the aniline dianilinodichlororthoquinone toward solvents is somewhat peculiar; from benzene alone it crystallizes unaltered, but a mixture of 5 parts of benzene with 1 of ligroin decomposes it into dianilinodichlororthoquinone and aniline. The probable explanation of these observations is that the aniline compound is dissociated by solution, and its 2 constituents recombine to form it once more, when both remain in the saturated solution, from which crystals are forming, whereas, the ligroin rendering the dianilinodichlororthoquinone insoluble, precipitates it, thus removing it from the possibility of reuniting with the dissolved aniline.

The conversion of the dianilinodichlororthoquinone,

$$C_6Cl_2(C_6H_5NH)_2O_2,$$

into dianilinochlorparaquinoneanil,

$$C_6HCl(C_6H_5NH)_2ONC_6H_5,$$

and of this latter body into the anil,

$$C_6H_2(C_6H_5NH)_2ONC_6H_5,$$

are noteworthy, because in these cases chlorine attached to a benzene ring has been replaced by hydrogen under the influence of hot aniline and alcohol, and this recalls the similar replacements of bromine or iodine in aromatic compounds under the influence of sodic alcoholates, sodic acetacetic ester, or sodic malonic ester, which have long been a subject of study in this laboratory. So far as we are aware only one other case is known in which chlorine has been replaced by hydrogen under such conditions. Gazzolo and one of us[1] obtained bromdiethoxydinitrobenzene from trichlorbromdinitrobenzene treated with sodic ethylate. In all other cases studied the chlorine either underwent a normal replacement, or remained unaltered. It is, therefore, an interesting point that the chlorine in this case is removed with much greater difficulty than bromine in the corresponding compound, for whereas the dianilinobromparaquinoneanil is deprived of its bromine by boiling with aniline and alcohol for 2–4 hours, the chlorine is fully replaced by hydrogen only after boiling for 3–4 days with the same mixture, and what makes this the more striking is that our other work with tetrachlororthoquinone, to be described in a later paper, shows that in substituted orthoquinones chlorine is much more easily replaced than bromine by radicals other than hydrogen. Whether this reduction of the halogen compound is due to the aniline, or to the alcohol, the aniline in this latter case acting only as a weak base, must be determined by further experiments.

---

[1] This Journal, **22**, 58 (1899).

The tetrachlororthoquinone also acted like the tetrabrom compound when it was treated with benzaldehyde, or acetone. Three compounds were formed in each case; a yellow, a red, identified as hexachlororthoquinopyrocatechin ether, and brown hexachlordihydroxypyrocatechin ether. Russe and one of us[1] found that the tetrabromorthoquinone with various ketones and aldehydes gave, in each case, only 3 products, the 2 hexabrom ethers, and the yellow hemiether,

$$C_6Br_4(OH)O.C_6Br_3O_2.$$

There is little doubt that our yellow product is the heptachlorhemiether, $C_6Cl_4(OH)O.C_6Cl_3O_2$, but it would be extremely difficult if not impossible to prove this, as even washing it with alcohol, or ligroin converts it into the ether,

$$C_6Cl_4O_2.C_6Cl_2O_2,$$

a result which is in harmony with our observation that chlorine is removed from these substituted orthoquinones more easily than bromine.

On one occasion, when an excess of chlorine was used in the preparation of tetrachlorpyrocatechin, we obtained what seemed to be a new quinone. Zincke and Küster,[1] under somewhat similar conditions, obtained the hexachlordiketotetrahydrobenzene, but our substance could not be identical with this, as it melted at 146°–147° instead of at 93°–94°, and a single chlorine determination indicated that it had the formula $C_6HCl_5O_2$. If this result is confirmed by further determinations it would be called pentachlordiketotetrahydrobenzene. We hope that the investigation of this substance may be continued in this laboratory in the near future.

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[1] This Journal, 36, 163 (1906).

EXPERIMENTAL.

Preparation of Tetrachlororthobenzoquinone.—The tetrachlorpyrocatechin used by us was prepared as follows, very nearly according to the method of Zincke:[2] Forty grams of pyrocatechin were dissolved in 200 cc. of glacial acetic acid in a 500 cc. flask, and treated with chlorine washed free from hydrochloric acid and dried with sulphuric acid. The stream of chlorine should not be too rapid, and the solution of pyrocatechin should be kept at temperatures below 30° by immersion in a vessel of water. If the process ran properly, the liquid took on a deep red color after 2 hours, and then the continued addition of the chlorine for a few minutes caused the mixture to become nearly solid, from the separation of crystals of tetrachlorpyrocatechin. These were filtered out, and the mother liquor treated again with chlorine, when a second crop of crystals was obtained, while a third treatment of the mother liquors with chlorine gave still another mass of crystals. The yield was nearly quantitative. It was purified by 2 crystallizations from glacial acetic acid, followed by washing with very dilute alcohol, or by crystallization from dilute alcohol, when it melted at 194°. If, in the foregoing preparation, the temperature of the solution was allowed to rise above 70° during the third hour of the addition of chlorine, its color changed from red to yellow, and hexachlororthodiketotetrahydrobenzene was formed. The tetrachlorpyrocatechin was converted into tetrachlororthoquinone by a method similar to that used by Koch and one of us[1] for making tetrabromorthoquinone. Thirty grams of tetrachlorpyrocatechin were dissolved in 200 cc. of glacial acetic acid with the aid of heat. The solution was then cooled by placing it in ice, until crystals began to form, when 11 grams of fuming nitric acid, diluted with 60 cc. of glacial acetic acid, were added gradually, and the mixture stirred rapidly for 90 seconds, after which it was diluted with 500 cc. of ice-cold distilled water, and thoroughly stirred again. In the course of 10 minutes bright red flakes of the quinone settled at the bottom of the beaker, when the supernatant liquid was siphoned off and the solid thrown upon a paper filter, supported in the funnel by a perforated porcelain plate covered with a thin asbestos mat, so that all the filtrations could be carried on by suction as rapidly as possible. After the mother liquor had been removed, the crystals were washed with 5 successive portions of 20 cc. of water, each wash water being thoroughly removed before adding the next, and then dried at 60°–70°, when they appeared as a bright red powder, melting at 133° to a dark red liquid. This melting point is higher than 129°–130°, that given by Zincke and Küster.[2] In this way 24.2 grams of tetrachlororthoquinone were obtained from 30 grams of tetrachlorpyrocatechin, *i. e.*, over 81 per cent of the theoretical yield. The success of this preparation was found to depend on the observance of the following conditions: Careful purification of the tetrachlorpyrocatechin, keeping the amounts of glacial acetic acid and water as small as possible, since the product is somewhat soluble in water, and rapid and complete filtration.

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[1] Ber. d. chem. Ges., **21**, 2723 (1888).

[2] *Ibid.*, **20**, 1770 (1887).

Hexachlororthoquinopyrocatechin ether, $C_6Cl_4O_2.C_6Cl_2O_2$.—This substance was prepared by the method[3] which had yielded the hexabrom ether. Eleven grams of tetrachlororthoquinone and 10 grams of tetrachlorpyrocatechin, dissolved in 300 cc. of glacial acetic acid by warming on the steam bath, were mixed with 150 cc. of water, and the mixture gently heated. The brilliant red precipitate formed in this way was filtered out, washed with alcohol, dried and found to weigh 13–14 grams, so that the yield of crude ether was about 76–80 per cent of the theoretical. It was purified by 2 crystallizations from nitrobenzene, when it showed the constant melting point 300°; it was then washed with alcohol to remove adhering nitrobenzene, and dried at 100° for analysis.

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[1] This Journal, **26**, 34 (1901). Zincke and Küster: Ber. d. chem. Ges., **21**, 2729 (1888).

[2] Ber. d. chem. Ges., **21**, 2729 (1888).

[3] Jackson and Koch: This Journal, **26**, 35 (1901).

0.1666 gram substance gave 0.3392 gram AgCl.

	Calculated for $C_6Cl_4O_2.C_6Cl_2O_2$.	Found.
Cl	50.59	50.34

Properties of Hexachlororthoquinopyrocatechin Ether.—It crystallizes from benzene, in which it is only sparingly soluble, in bright red needles; from nitrobenzene in red, truncated pyramids, but its color is lighter than that of the corresponding bromine compound. It melts at 300°, and is slightly soluble in most of the organic solvents. The best solvent for it is nitrobenzene, but the solution must not be heated much above 100°, as at high temperatures the ether is decomposed with the formation of a brown product. The strong mineral acids have no effect on it, but sodic or potassic hydrate converts it into the corresponding salt of chloranilic acid. Aqueous ammonia converts it into a substance deposited in black needles. Aniline gave the same products with it as with the tetrachlororthoquinone which are described later in this paper.

Hexachlororthodihydroxypyrocatechin Ether, $C_6Cl_4O_2.C_6Cl_2(OH)_2$.—Ten grams of the hexachlororthoquinopyrocatechin ether were reduced with 3 per cent sodium amalgam and water in a flask kept full of carbonic dioxide. After the reaction had run at ordinary temperatures for several days, the red quino ether had been converted into a white product, which, however, turned purple on exposure to the air. The dark colored alkaline filtrate gave marked tests for a pyrocatechin. The solid product was purified by washing successively with dilute hydrochloric acid and alcohol, and then crystallizing it from a mixture of equal parts of benzene and alcohol, till it showed the constant melting point of 290°, when it was dried at 100° for analysis:

I. 0.1986 gram substance gave 0.4019 gram AgCl.
II. 0.0590 gram substance gave 0.1211 gram AgCl.

	Calculated for $C_6Cl_4O_2.C_6Cl_2(OH)_2$.	Found.	
		I.	II.
Cl	50.36	50.03	50.74

Properties of Hexachlororthodihydroxypyrocatechin Ether.—It crystallizes in needles which differ in color according to the solvent used; from alcohol they are white, from a mixture of equal parts of alcohol and benzene a delicate heliotrope-purple, from nitrobenzene chocolate-brown. It melts at 290°, that is, at a decidedly lower temperature than the corresponding bromine compound; and is also distinctly more soluble than that, although only slightly soluble in all the common organic solvents except nitrobenzene. The best solvent for it is a mixture of equal parts of alcohol and benzene. Fuming nitric acid converts it quantitatively into the red hexachlororthoquinopyrocatechin ether. Sodic hydrate has a very slight solvent effect, but turns the undissolved crystals deeper purple.

Action of Aniline on Tetrachlororthoquinone.[1]—Five grams of tetrachlororthoquinone, dissolved in 100 cc. of alcohol, were added, in small portions at a time, to a cold solution of 7.5 grams of aniline in 100 cc. of alcohol, the mixture being thoroughly stirred after each addition. Under these conditions a voluminous, light brown precipitate of anilinedianilinodichlororthoquinone was formed, which was filtered out, after half the solution of quinone had been added. The remaining half of the solution of quinone was then added to the red filtrate, and stirred vigorously. At first a thick, dark greenish mass was formed, but, as the stirring continued, the color became lighter until the solid was changed into small, glistening, yellow flakes of the ethyl alcohol-dianilinodichlororthoquinone, which were also filtered out. This second filtrate was allowed to stand for several hours, or warmed for a short time, when it deposited black crystals of dianilinochlorparaquinoneanil, or it was boiled under a return condenser for 3 or 4 days, which formed the dark brown needles of dianilinoparaquinoneanil. The same change took place with the bromine compound by boiling for only 2 to 4 hours.

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[1] Jackson and Porter: THIS JOURNAL, 30, 518 (1903).

Dianilinodichlororthobenzoquinone, $C_6Cl_2(C_6H_5NH)_2O_2$.—This substance was not a direct product of the action of tetrachlororthoquinone on aniline, but was obtained from the bulky brown precipitate of its aniline compound made as described above. For this purpose it was dried in the air and then heated with a mixture of 5 parts of benzene and 1 of ligroin, which changed its color to reddish purple in a few minutes. The undissolved purple crystals were filtered out, and treated 3 times in the same way, with fresh portions of the mixture of 5 parts of benzene and 1 of ligroin. Finally, it was purified by crystallization from a large amount of this same mixture, until it showed the constant melting point 194°–195°, when it was dried for analysis. The decomposition of the aniline compound, $C_6Cl_2(C_6H_5NH)_2O_2.C_6H_5NH_2$, was brought about apparently by the slight solubility of the dianilino body and the easy solubility of the aniline in the mixture of benzene and ligroin; it is, therefore, necessary to repeat the treatment several times with fresh portions of the mixture to insure complete decomposition. The filtrates contained aniline and a little of the brown aniline compound.

0.1891 gram of substance gave 0.1491 gram AgCl.

	Calculated for $C_6Cl_2(C_6H_5NH)_2O_2$.	Found.
Cl	19.77	19.49

Properties of Dianilinodichlororthoquinone.—It crystallizes from a mixture of benzene and ligroin in reddish purple, tapering needles, which melt at 194°–195°. It is easily soluble in benzene, slightly soluble in ligroin. The best solvent for it is the mixture of 5 parts of benzene with 1 of ligroin. Strong hydrochloric acid acts on it slightly; strong nitric acid dissolves it with decomposition; strong sulphuric acid gives a greenish solution with it; sodic hydrate dissolves it with decomposition. It was easily reduced with zinc dust and acetic acid to a substance which gave tests for a pyrocatechin, but was not further studied. Its most characteristic property is its strong tendency to form addition compounds. Those with aniline and with ethyl alcohol are described below.

Aniline Dianilinodichlororthobenzoquinone, $C_6Cl_2(C_6H_5NH)_2O_2.C_6H_5NH_2$.—This substance was the light brown precipitate obtained as the first product of the reaction of tetrachlororthoquinone with aniline, in alcoholic solution. It was also made by boiling a benzene solution of the dianilinodichlororthoquinone with the calculated quantity of aniline. In either case the substance was purified by recrystallization from benzene, until it showed the melting point 164°–165°, when it was dried *in vacuo* for analysis. It seems strange that this substance should crystallize unaltered from benzene, when it is decomposed by solution in a mixture of 5 parts of benzene and 1 of ligroin. An attempt has been made to explain this phenomenon in the introduction.

I. 0.1413 gram substance gave 0.0930 gram AgCl.
II. 0.1864 gram substance gave 0.1234 gram AgCl.

	Calculated for $C_6Cl_2(C_6H_5NH)_2O_2.C_6H_5NH_2$.	Found. I.	Found. II.
Cl	15.71	16.28	16.37

Properties of Aniline Dianilinodichlororthoquinone.—It crystallizes from boiling benzene in long, fine, light brown needles, which melt, with decomposition, at 164°–165°. It is soluble to a certain extent in all the common organic solvents, from some of which, like benzene, it is deposited unaltered, while from others the dianilinodichlororthoquinone separates, and aniline is left in solution. This decomposition seems to be produced by solvents in which the dianilino body is but slightly soluble. A mixture of benzene and ligroin shows this reaction excellently. The free aniline was identified in the benzene-ligroin mother liquor by the formation of a soluble hydrochloride with hydrochloric acid, and the phenylisonitrile test. Strong hydrochloric or nitric acid dissolves and decomposes it, strong sulphuric acid forms with it a green solution; sodic hydrate, in hot aqueous solution, decomposes it.

Ethyl Alcohol Dianilinodichlororthobenzoquinone, $C_6Cl_2(C_6H_5NH)_2O_2.C_2H_5OH$.—This substance is the yellow product formed by the action of tetrachlororthoquinone on aniline, as described above. It was also prepared by allowing dianilinodichlororthoquinone, or its addition compound with aniline to stand for several days in contact with cold alcohol. In either case it was purified by crystallization from warm alcohol, until it showed the constant melting point 140°–141°, when it was dried *in vacuo* for analysis:

0.1032 gram substance gave 0.0734 gram AgCl.

	Calculated for $C_6Cl_2(C_6H_5NH)_2O_2.C_2H_5OH$.	Found.
Cl	17.53	17.58

Properties of Ethyl Alcohol Dianilinodichlororthoquinone.—It crystallizes from warm alcohol in plates of a chrome yellow color, which melt, with decomposition, at 140°–141°. It dissolves easily in alcohol, ether, benzene, toluene, or acetone; very slightly soluble in ligroin. A boiling mixture of 5 parts of benzene and 1 of ligroin decomposes it with the formation of the dianilinodichlororthoquinone. It is easily soluble in the strong mineral acids, or in sodic hydrate.

Dianilinochlorparaquinoneanil, $C_6HCl(C_6H_5NH)_2ONC_6H_5$.—This substance was the third product of the action of tetrachlororthoquinone on an alcoholic solution of aniline. It is more stable than the 3 compounds just described; and was also prepared by boiling any one of these with an alcoholic solution of aniline, but the boiling must not be too long continued, as in that case some dianilinoparaquinoneanil will be formed. The black shining crystals, prepared by any of these methods, were purified by crystallization from a mixture of equal parts of benzene and methyl alcohol, until they showed the constant melting point 180°, when they were dried for analysis:

0.1368 gram substance gave 0.0484 gram AgCl.

	Calculated for $C_6HCl(C_6H_5NH)_2ONC_6H_5$.	Found.
Cl	8.88	8.75

Properties of Dianilinochlorparaquinoneanil.—It crystallizes from a mixture of benzene and methyl alcohol in brilliant black, flattened, blunt needles, which melt at 180°. It is easily soluble in benzene, toluene, acetone, ethyl acetate, or glacial acetic acid; less soluble in ethyl or methyl alcohol, or in ether; slightly soluble in ligroin. The best solvent for it is a mixture of equal parts of benzene and methyl alcohol. It dissolves in hot strong hydrochloric acid with a green color; strong nitric acid dissolves it with decomposition; strong sulphuric acid dissolves it with a dark purple color. This indicates that the substance does not belong to the ortho series as the orthoquinones described above gave a green color with sulphuric acid. A strong solution of potassic hydrate has no apparent effect on it whether hot or cold. The reasons for believing it to belong to the para series, in addition to the color reaction with sulphuric acid already mentioned, are that it shows no tendency to form addition compounds, a specimen undergoing no change even after standing with methyl alcohol for 2 weeks, and its easy conversion into the known dianilinoparaquinoneanil, which was brought about by treating its ethereal solution with sulphurous dioxide. The same change was produced by boiling the substance with aniline and alcohol for 3 to 4 days, but this last observation is of no use in determining its constitution, as during this long action an ortho derivative might well have passed over into the para series.

Dianilinoparaquinoneanil, $C_6H_2(C_6H_5NH)_2ONC_6H_5$. — This substance was obtained by boiling for 3–4 days, under a reverse condenser, the last filtrates formed in working up the products of the action of tetrachlororthoquinone on aniline dissolved in alcohol, or boiling any of the dianilino compounds just described with aniline and alcohol, or by treating an ethereal solution of dianilinochlorparaquinoneanil with sulphurous anhydride. To purify the product it was washed with cold ethyl alcohol and then recrystallized from a mixture of benzene and methyl alcohol. This substance was discovered by Zincke and Hagen,[1] who made it by the action of aniline, dissolved in acetic acid, on paraquinone. They give the melting point as 202°–203°, but, as was also observed by Porter and one of us,[2] it is a very difficult matter to raise the melting point beyond about 198°. Accordingly, we identified it by comparing our specimen with one made by Porter from paraquinone by Zincke and Hagen's method and one made by him from tetrabromorthoquinone. All three of these specimens were recrystallized from a mixture of equal parts of benzene and methyl alcohol, when they all showed the same color and characteristic comb-like crystals, the melting point 198°, and the same color reactions, blue with strong hydrochloric acid, brown with nitric acid, and reddish brown with strong sulphuric acid. There can be no doubt, therefore, of the identity of our product.

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[1] Ber. d. chem. Ges., **18**, 785 (1885).

[2] THIS JOURNAL, **30**, 534 (1903).

Pentachlordiketotetrahydrobenzene, $C_6HCl_5O_2$?—When an excess of chlorine was added to the acetic acid filtrates from the preparation of tetrachlorpyrocatechin, the liquid turned red, and after standing for 7 months deposited long, brass-colored needles, which were recrystallized from glacial acetic acid and dried at 100° for analysis.

0.1540 gram substance gave 0.3927 gram AgCl.

	Calculated for $C_6HCl_5O_2$.	Found.
Cl	62.84	63.06

As we made only this single analysis of the substance, its nature cannot be considered settled, but in accordance with this result it may be called, provisionally, pentachlordiketotetrahydrobenzene.

Properties.—It crystallizes from glacial acetic acid in brassy yellow, hexagonal plates with a brilliant luster, which melt at 146°–147° to a brown liquid. It is hoped that the investigation of this substance can be taken up in this laboratory in the near future.

Work on the action of benzaldehyde, or acetone on tetrachlororthoquinone, is described in the introduction to this paper.

CAMBRIDGE, MASS.,
Aug. 3, 1906.

Contribution from the Kent Chemical Laboratory of the University of Chicago.

ON ALDOL, PENTAERYTHROSE AND THE ACTION OF COPPER ACETATE ON THE HEXOSES.

BY A. F. MCLEOD.

All the condensation reactions shown by aldehydes in the presence of alkalies have been classified by Nef[1] under the head of olefine and alkylidene condensations.

It is now possible, in the light of Nef's work on aldehydes, alcohols, etc., during the past 12 years[2] and because of some observations of my own on acetaldehyde which were made at Dr. Nef's suggestion and under his guidance, to formulate these reactions more precisely. An aqueous solution of an aldehyde contains the following substances in dynamic equilibrium:

$$\underset{\text{Aldehyde.}}{RHC:O + H_2O} \rightleftarrows \underset{\text{Alkylidene dihydroxide.}}{RHC(OH)_2} \rightleftarrows \underset{\text{Hydroxyalkylidene.}}{\underset{\diagup\diagdown}{RCOH}} + H_2O.$$

$$[R = C_nH_{2n+1}, C_6H_5 \text{ or } H.]$$

Now it is well known that an aldehyde, in aqueous solution, never goes over into its condensation products at temperatures between 20° and 100°; polymerization of the active aldehyde molecules,

$$3RH\underset{|}{C}-\underset{|}{O} \rightleftarrows (RH\underset{|}{C}-\underset{|}{O})_3,$$

on the other hand, may often take place spontaneously.

When we treat an aldehyde with an aqueous solution containing an alkali or an alkaline salt, *e. g.*, caustic or mild alkalies, potassium cyanide, sodium or potassium formate or acetate, etc., condensation often takes place at once in the cold even in the presence of a marvelously small amount of the reagents named. What is the function of the alkali in these cases and how may its concentration affect the end result? The aldehydes in the form of their hydrates are $RHC(OH)_2$, the alkylidene dihydroxides are really diatomic alcohols; they must, therefore, possess, like all alcohols, weak acid properties and be capable of salt formation;[1] and the exhaustive experiments of Nef on the monatomic as well as on the polyatomic alcohols have shown conclusively that the salts of all primary and secondary alcohols are relatively much more dissociated into alkylidene,

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[1] Ann. Chem. (Liebig), **298**, 219–223.

[2] *Ibid.*, **298**, 202–374; **309**, 126–189; **310**, 316–335; **318**, 1–57, 137–230; **335**, 191–333.

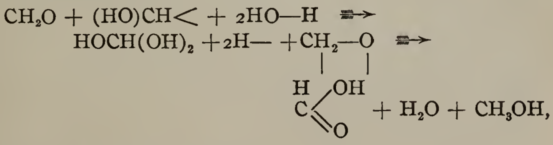
$$RR'CHOM \rightleftarrows RR'C< + HOM,$$

than the corresponding free alcohols. It is, therefore, self-evident that an aldehyde in the presence of an alkaline salt, or even of powdered calcium carbonate at 100°,[2] must be *relatively more* dissociated into hydroxyalkylidene,

$$R(HO)CHOM \rightleftarrows R(HO)C< + HOM.$$

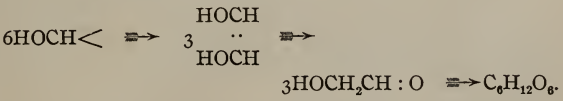
As soon as the concentration of the hydroxyalkylidene reaches a certain definite limit, a condensation reaction, or a decomposition of the water present by the hydroxyalkylidene must take place. Often both reactions occur simultaneously.

Thus, according to unpublished observations of Nef, when 4 liters of 1 per cent aqueous formaldehyde are treated, in the cold, with 24 grams of powdered quicklime, 80 per cent of the reaction proceeds slowly according to

(I) 

$$CH_2O + (HO)CH< + 2HO{-}H \rightarrow HOCH(OH)_2 + 2H{-} + \begin{array}{c}CH_2{-}O\\ |\qquad |\\ H\quad OH\end{array} \rightarrow HC\begin{smallmatrix}OH\\ O\end{smallmatrix} + H_2O + CH_3OH,$$

and only 20 per cent according to

II. 

$$6HOCH< \rightarrow 3\begin{array}{c}HOCH\\ \cdot\cdot\\ HOCH\end{array} \rightarrow 3HOCH_2CH:O \rightarrow C_6H_{12}O_6.$$

If, on the other hand, small amounts of lead hydroxide,[3] or powdered calcium carbonate[4] be used in place of lime, then reaction II., *i. e.*, sugar formation, is the chief reaction. The remarkable difference in the result is obviously simply due to the fact that the concentration of hydroxymethylene, present in Lobry de Bruyn's and in Euler's experiments, is *far smaller* than when lime, or some other caustic alkali is used; consequently polymerization of 2 hydroxymethylene molecules to dihydroxyethylene which then goes over spontaneously into glycolyl aldehyde, etc., is the chief reaction in the former case. Similarly 2 molecules of hydroxyphenylmethylene, $C_6H_5\underset{\wedge}{C}OH$, formed from benzylidenedihydroxide by dissociation, polymerize[1] to dihydroxystilbene, $\begin{matrix}C_6H_5COH\\ \cdot\cdot\\ C_6H_5COH\end{matrix}$, which then spontaneously transforms itself, probably, without an intermediate addition of water, into benzoin, $C_6H_5C : OCH(OH)C_6H_5$. In the case of benzaldehyde the benzoin condensation (*i. e.*, reaction II.) is possible only by using small amounts of potassium cyanide, which here obviously serves a double purpose, first in increasing the amount of methylene dissociation and second in uniting temporarily with the hydroxyphenylmethylene to form an easily dissociable double salt, $C_6H_5(HO)C : CNK$, analogous to the double cyanides and fulminates.[2] When, on the other hand, benzaldehyde is treated with cold, concentrated, aqueous potassium hydroxide, molecular amounts of benzyl alcohol and benzoic acid are formed according to reaction I. It should be *especially emphasized* that only *tertiary* aldehydes, such as benzaldehyde, trimethylacetaldehyde, $(CH_3)_3 \vdots CCH : O$, etc., *i. e.*, those which contain the aldehyde group bound to a carbon atom which is free from hydrogen can undergo the benzoin condensation—which is simply due to a polymerization of two hydroxyalkylidene molecules,

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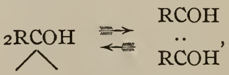
[1] Nef: Ann. Chem. (Liebig), **318**, 138–187; **335**, 312. Cf. Euler: Ber. d. chem. Ges., **39**, 36–45.

[2] Euler: Ber. d. chem. Ges., **39**, 45.

[3] Lobry de Bruyn and Ekenstein: Rec. Trav. Chim., **18**, 309.

[4] Euler: Ber. d. chem. Ges., **39**, 45.



$$2R\underset{\wedge}{C}OH \rightleftarrows \begin{matrix}RCOH\\ \cdot\cdot\\ RCOH\end{matrix},$$

etc. The conversion of formaldehyde into glycollic aldehyde must, however, also be considered as a benzoin condensation. Why is it that the ordinary aliphatic aldehydes do not undergo an analogous benzoin condensation on treatment with alkaline reagents? The reason for the well-known difference in behavior is easily understood on the basis of the following considerations which have been presented for some years past by Dr. Nef in his lectures on organic chemistry, and which are simply an application of his ideas on the laws of condensation presented in a paper of his.[1] A primary or a secondary aldehyde, $RCH_2CH:O$ and $(RR')CHCH:O$, still contains on the carbon atom holding the CHO group one or more easily dissociable non-ionic hydrogen atoms.

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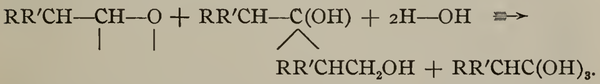
[1] Nef: Ann. Chem. (Liebig), 298, 312.

[2] Nef: *Ibid.*, 280, 334-338; 298, 313. Cf. Goldthwaite: THIS JOURNAL, 30, 466, foot-note.

When, therefore, the concentration of the hydroxyalkylidine molecules is in these cases increased by the addition of a mild or caustic alkali, or an alkaline salt, the following 2 entirely independent reactions may take place simultaneously or singly:

(I.) Decomposition of the water, or caustic alkali present by the hydroxyalkylidene according to



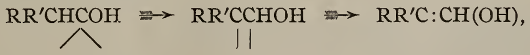
$$RR'CH-\underset{|}{C}H-\underset{|}{O} + RR'CH-\underset{\wedge}{C}(OH) + 2H-OH \rightleftharpoons RR'CHCH_2OH + RR'CHC(OH)_3.$$

Reaction I. is, therefore, common to all aldehydes, whether primary, secondary or tertiary; the Dumas-Stas reaction, whereby all aldehydes are converted quantitatively by potash-lime at 200°–250°, into hydrogen and the potassium salt of the corresponding fatty acid,

$$RCH:O + KOH \rightleftharpoons RCOOK + H_2,$$

is obviously simply a special phase of reaction I.

(II.) The hydroxyalkylidene may transform itself, by intramolecular addition,[2]

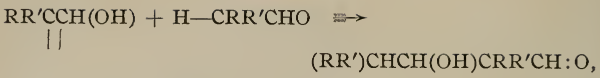


$$RR'CH\underset{\wedge}{C}OH \rightleftharpoons RR'\underset{\|}{C}CHOH \rightleftharpoons RR'C:CH(OH),$$

into an olefine derivative, which then at once unites with the unchanged aldehyde present, according to

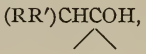
[1] Ann. Chem. (Liebig), **298**, 202–374.

[2] Nef: *Ibid.*, **318**, 1–57; **335**, 196–200.



$$\mathrm{RR'}\underset{||}{\mathrm{C}}\mathrm{CH(OH)} + \mathrm{H—CRR'CHO} \rightarrow \mathrm{(RR')CHCH(OH)CRR'CH{:}O},$$

giving an aldol (olefine condensation). The aldols thus formed may then give in many cases, by further loss of water, olefine derivatives, *e. g.*, acetaldol goes over, in the presence of traces of alkali or acid, with remarkable ease, by loss of water, into crotonaldehyde, in 2 stages, see below. A polymerization of 2 hydroxyalkylidene molecules,



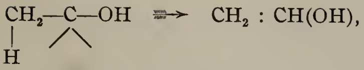
$$\mathrm{(RR')CH}\underset{\wedge}{\mathrm{C}}\mathrm{OH},$$

to a benzoin-like body,

$$\mathrm{RR'CHC(OH){:}C(OH)CHRR'} \rightarrow \mathrm{RR'CHCOCH(OH)CHRR'},$$

which is also possible from a theoretical standpoint in the case of primary and secondary aldehydes has, up to the present time, never been observed; such a transformation is, indeed, highly improbable because of the ease with which the intramolecular addition reaction II., just cited, must take place as soon as the concentration of the hydroxyalkylidene present is above a definite limit. It is, however, not impossible that in the future certain primary and secondary aldehydes may be found which, in addition to the ordinary aldol condensation, may also undergo a benzoin condensation.

In studying the action of caustic alkalies and alkaline carbonates on acetaldehyde I have, moreover, made the following important observation: When the concentration of alkali used is below a certain definite limit, which is 0.1 per cent in the case of sodium and calcium hydroxides, no appreciable condensation of the acetaldehyde to aldol or crotonaldehyde takes place, even after weeks of standing at ordinary temperatures. This is just what one would expect from the theory presented above, a certain definite amount of alkali is obviously necessary in order to increase the concentration of the hydroxyethylidene molecules in quantity sufficient to enable the transformation into vinyl alcohol,



$$\underset{\substack{|\\ H}}{CH_2}\text{—}\underset{\wedge}{C}\text{—}OH \Longrightarrow CH_2 : CH(OH),$$

to take place, and this is a condition *sine qua non* in Nef's theory of aldol condensation. Nef has shown, furthermore, that when freshly precipitated oxide of mercury is present the vinyl alcohol first set free by the addition of alkalies is prevented from uniting with unchanged aldehyde to give aldol because it unites *by preference* with the metallic oxide introduced into the system[1] to form an insoluble white salt, which readily gives back acetaldehyde on treatment with dilute acids.

Finally, it is well known from Lieben's experiments that when molecular mixtures of various aliphatic aldehydes are treated with alkalies, only one of the two theoretically possible mixed aldols is formed; thus acetaldehyde gives, with isobutyric aldehyde, only

$$\text{(I.)}\ CH_3CH(OH)C(CH_3)_2CH : O,$$

and not a trace of

$$\text{(II.)}\ (CH_3)_2CHCH(OH)CH_2CH : O.$$

This can only be due to the fact that acetaldehyde is converted into vinyl alcohol far more readily and with much smaller concentration of the alkali than is isobutyric aldehyde into the corresponding vinyl alcohol homologue, $(CH_3)_2:CCH(OH)$; consequently, vinyl alcohol absorbs isobutyric aldehyde to give product I.

The fact that remarkably different minimal concentrations of alkali are required in the case of the various aldehydes in order that a transformation according to II., *i. e.*, a benzoin or aldol condensation may take place, is of the utmost importance in synthetic work. Thus it is clear that when aqueous mixtures of acetaldehyde and formaldehyde are treated with potassium or sodium hydroxides, taking care to keep the concentration of the alkali used below 0.1 per cent, no trace of aldol or crotonaldehyde can be formed; the formaldehyde, on the other hand, which is by far the most sensitive of all the aldehydes towards alkalies and is even condensed in the presence of calcium carbonate to hexoses, must contain, under the conditions named, a sufficiently large concentration of hydroxymethylene molecules to form at once with the acetaldehyde present a mixed aldol. Tollens[1] has, in fact, shown that one can obtain large amounts of pentaerythrite, $\mathrm{C} \vdots (\mathrm{CH_2OH})_4$, from aqueous solutions of acetaldehyde and formaldehyde (4 mols.) in the presence of calcium hydroxide. It is evident, from Nef's work, that this reaction proceeds through the following 5 successive stages:

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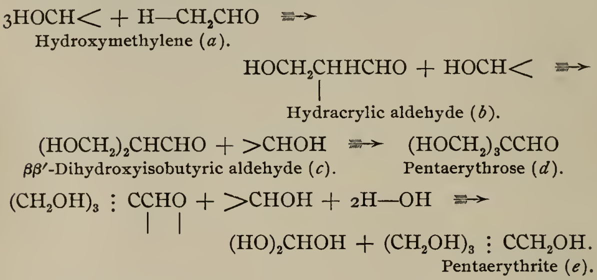
[1] Ann. Chem. (Liebig), 298, 316-318.



$$3\mathrm{HOCH}< + \mathrm{H{-}CH_2CHO} \rightarrow$$

Hydroxymethylene (*a*).

$$\mathrm{HOCH_2\underset{|}{C}HHCHO} + \mathrm{HOCH}< \rightarrow$$

Hydracrylic aldehyde (*b*).

$$(\mathrm{HOCH_2})_2\mathrm{CHCHO} + >\mathrm{CHOH} \rightarrow (\mathrm{HOCH_2})_3\mathrm{CCHO}$$

ββ'-Dihydroxyisobutyric aldehyde (*c*). Pentaerythrose (*d*).

$$(\mathrm{CH_2OH})_3 : \mathrm{C\underset{|}{C}\underset{|}{H}O} + >\mathrm{CHOH} + 2\mathrm{H{-}OH} \rightarrow$$

$$(\mathrm{HO})_2\mathrm{CHOH} + (\mathrm{CH_2OH})_3 : \mathrm{CCH_2OH}.$$

Pentaerythrite (*e*).

I have consequently taken up, at Dr. Nef's wish, a renewed study of the action of alkalies on mixtures of acetaldehyde and formaldehyde with the object of proving, by experiment, that the reaction takes place through the stages indicated; it was *a priori* improbable that an intermediate formation of hydracrylic aldehyde (*b*), or even of ββ'-dihydroxyisobutyric aldehyde (*c*) could be proved by direct means, since the non-ionic α-hydrogen atoms still left bound to the carbon atom containing the CH:O group in these intermediate products must be *relatively* far more dissociated from carbon than the corresponding ones in acetaldehyde; consequently these substances must, in the main, be at once absorbed by more hydroxymethylene to give pentaerythrose (*d*).

I succeeded, therefore, in obtaining large amounts of pentaerythrose in the reaction under discussion; and the indications point also to the presence of relatively large amounts of ββ'-dihydroxyisobutyric aldehyde (*c*) in the crude material obtained. That the reaction proceeds through stage (*b*) was, furthermore, definitely established because mixtures of hydracrylic aldehyde, which has recently been discovered by Nef, and of formaldehyde (2 mols.) give, when treated with traces of sodium hydroxide, an almost quantitative yield of crude pentaerythrose.

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[1] Ann. Chem. (Liebig), 265, 316; 276, 58.

EXPERIMENTAL PART.

It is clear from a study of the literature on the subject that acetaldehyde, when treated with mild or caustic alkalies, or with concentrated sulphuric acid, is transformed successively into aldol, crotonaldehyde, oily volatile and non-volatile condensation products of crotonaldehyde and, finally, into aldehyde resin; the constitution, or even the homogeneous character of the 3 last-named products, has not yet been ascertained.

The following experiments with acetaldehyde prove that when the concentration of the mild or caustic alkali used is below a certain definite limit, no condensation of the acetaldehyde takes place even on 6 weeks' standing at ordinary temperatures; furthermore, the conditions under which the best yield of aldol and of crotonaldehyde can be obtained from acetaldehyde were thoroughly investigated. It was definitely established that aldol, as well as crotonaldehyde, never gives back a trace of acetaldehyde on treatment with water, with very dilute alkalies, or with acids in sealed tubes at 100°. Aldol goes over, under these conditions with the greatest ease, into crotonaldehyde, which is, in turn, converted into insoluble, yellow, volatile and non-volatile oils and, finally, into aldehyde resin.

Manufacture of Acetaldehyde and Its Behavior towards Dilute Alkalies.

Since preparations of acetaldehyde invariably contain a greater or less proportion of paraldehyde, all the acetaldehyde used in my experiments was prepared from paraldehyde by dissociation. A few drops of concentrated sulphuric acid have been usually used for this purpose, but there is always considerable loss through charring by this process. The following method is thoroughly reliable and always gives at least a 90 per cent yield. Paraldehyde, 212.2 grams, and 20 per cent sulphuric acid, 10 cc., are mixed and heated in a flask provided with a Glinsky apparatus. The temperature of the surrounding bath is kept at 85°–95°, whereupon acetaldehyde rapidly distils over; on redistillation, 190.4 grams of aldehyde, b. p. 21°–27°, were regularly obtained. Ten grams of aldehyde were dissolved in the cold in 10 cc. of saturated lime water, proved by titration with standard acid to contain 0.01617 gram of calcium hydroxide; the mixture was then allowed to stand at room temperature for 6 weeks. On heating the alkaline solution on a boiling water-bath and subsequently drying the distillate with calcium chloride, 8.4 cc. of aldehyde, b. p. 21°–30°, were recovered unchanged. This is 67.2 per cent of the amount originally taken.

A second experiment, in which 10 grams of aldehyde and 10 cc. of 0.1 per cent sodium hydroxide, containing, as determined by titration with standard acid, 0.01154 gram of sodium hydroxide, were used, gave the following result: After standing for 21 days at room temperature no trace of coloration or of formation of insoluble aldehyde resin could be observed. The alkaline solution was now heated on a boiling water-bath to drive off the unchanged aldehyde, proceeding as in the first experiment. Seven and eight-tenths cc. of aldehyde, b. p. 21°–30°, were recovered. Furthermore, titration of the aqueous alkaline solution, left after distilling off the aldehyde, with standard acid proved that 0.0112 gram of sodium hydroxide was still present, only 0.3 milligram, therefore, had been used up. These experiments prove that when the concentration of the calcium or sodium hydroxide solutions is 0.1 per cent no condensation or only exceedingly slow condensation of acetaldehyde takes place. It is very probable that 0.2 per cent sodium or potassium carbonate solutions will have no condensation effect on aldehyde. I expect, moreover, to continue experiments in this direction at once, in the autumn, including also a study of the action of such substances as potassium cyanide, sodium and potassium acetate, etc.

Manufacture of Aldol and of Crotonaldehyde, and Behavior of These Substances towards Water, Dilute Alkalies and Acids, Etc.

The only 2 satisfactory methods of preparing aldol in quantity are those of Halpern[1] and of Orndorff and Newbury[2] from acetaldehyde and small amounts of powdered potassium carbonate, or 10 per cent aqueous potassium carbonate, respectively. In both cases the yield of pure distilled aldol obtained was never over 50 per cent of that demanded by theory. I have always obtained a large and practically constant yield, 60 per cent, of aldol by the following method, which is essentially that of Orndorff and Newbury.

A solution of 47 grams of aldehyde in 20 grams of water was treated, in the cold, with 2 grams of potassium carbonate, dissolved in the smallest possible amount of water. The temperature was kept below 10° for the first half hour and the mixture was then left standing, at ordinary temperatures, for 18 hours. The aldol was removed from the aqueous solution by extracting 3 times with ether. After drying with calcium chloride, and removing the last traces of ether by heating in a flask, up to 80° (20 mm.), 41 grams of crude, yellowish aldol were obtained. This gave, on distillation, 28.3 grams of the pure product boiling at 79° (20 mm.) and only 5.1 grams of higher boiling oil remained in the distilling flask. Considerable loss, 15–20 per cent, must, therefore, have occurred through volatilization. Two further experiments, carried out in practically the same manner, and with the same amount of material, gave, after 1 distillation, 48–50 per cent of pure aldol and 20–35 per cent of higher boiling oils.

Another experiment with 20 grams of aldehyde, 8 grams of water and 1 gram of potassium carbonate gave, after 18 hours' standing, by acidifying with the calculated amount of hydrochloric acid and then heating on a boiling water-bath, 3 cc. of aldehyde, boiling at 21°–35°; this proves that about 12 per cent of the aldehyde is left unchanged in the process used. Nevertheless, it is not advisable to allow the alkaline solutions to stand longer than 18 hours, to insure complete transformation of the aldehyde, because aldol itself is rapidly acted upon under the conditions employed, as was also proved by special experiments. Thus it was observed that when the alkaline solution stood longer, 48 hours for example, instead of 18, only 20–30 per cent, or even less, of pure aldol was obtained and the amount of non-volatile and higher-boiling yellowish oil was correspondingly increased. Special experiments have also shown that it is impossible to obtain aldol in appreciable quantity from aldehyde either by means of traces of powdered potassium hydroxide or by using aqueous solutions of this substance in concentration varying from 0.1 per cent to 2 per cent.

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[1] Monats. Chem., **13**, 517.

[2] *Ibid.*, **22**, 59.

In order, finally, to obtain crotonaldehyde in quantity for investigation it was found, after repeated trial of various methods given in the literature, that the following process gives by far the best yield: Crude aldol, made from aldehyde and 10 per cent potassium carbonate, as stated above, is mixed with 0.5 of its weight of powdered potassium bisulphate and heated rapidly first at 120°–130° and finally in a bath at 180°–200.° The distillate, after separating from small amounts of water and drying with calcium chloride, boils at once at 98°–106°. The yield was found to be regularly 70–73 per cent of that demanded by theory.

My experience with Lieben's method[1] for making crotonaldehyde was as follows: A mixture of 15 cc. of acetaldehyde and 5 cc. of 28 per cent sodium acetate was heated for 10 hours, in a sealed tube, at 100°. On working up by heating first in a bath at 100° and then at 120°–130°, etc., 9 cc. of acetaldehyde, 2.4 cc. of crotonaldehyde, boiling at 98°–106° and 1.2 grams of yellow, mobile oil, boiling at 90°–120° (24 mm.) were obtained. Similar mixtures of aldehyde and sodium acetate, when heated longer at 100°, *e. g.*, for 36 hours, gave only small amounts of unchanged aldehyde and of crotonaldehyde. The main product was an insoluble, reddish, mobile oil which, on fractionation (20 mm.), boils in part at 90°–120° and leaves much non-volatile, viscous, red gum—obviously condensation or polymerization products of crotonaldehyde. Finally, Orndorff and Newbury's method of making crotonaldehyde,[2] by direct heating of aldol under ordinary pressures, gave, under the most

[1] Monats. Chem., 13, 519.

[2] *Ibid.*, 13, 517.

favorable conditions, only a 37.5 per cent yield of the product. Thus 13.5 grams of aldol, boiling at 79° (20 mm.), when heated in a flask connected with a Glinsky apparatus, a condenser, and well-cooled receiver, gave, finally, after heating in a bath from 190°–220°, 0.4 gram of aldehyde, boiling at 21°–30°, 4 grams of crotonaldehyde, boiling at 102°–106°, and 4 grams of much higher boiling yellow oil remained in the distilling flask. Furthermore, 11 grams of aldol, heated for 6 hours in a sealed tube at 180°–200°, gave an entirely similar result. An exceedingly good method for making crotonaldehyde is simply to heat aldol with 12 parts of water for 14 hours, in a sealed tube, at 100°; a 73 per cent yield is regularly obtained. No trace of aldehyde, but small amounts of yellow crotonaldehyde condensation products are also formed in this case. The separation of crotonaldehyde from water involves on difficulty, as on distillation of an aqueous solution the aldehyde comes over entirely with small amounts of water in the first portion of the distillate. The first fraction is, therefore, simply redistilled, or is often freed at once from small amounts of water by drying with calcium chloride, etc.

A solution of 6.4 grams of crotonaldehyde, b. p. 103°–104°, in 70 cc. of water, was heated in a sealed tube, at 100°, for 43 hours, with the following result: Three cc. of dry crotonaldehyde, boiling at 98°–103°, were recovered unchanged. On extracting the aqueous solution with ether, etc., only 0.5 gram of yellowish oil was obtained, one-half of which boiled from 84°–86° (29 mm.) and the remainder was non-volatile. It is possible that the small amount of volatile oil obtained was aldol but, unfortunately, we have no means of sharply identifying aldol by conversion into a crystalline derivative. In any case, the results obtained show that the behavior of aldol and crotonaldehyde towards water is in marked contrast to that of the lower homologues, hydracrylic aldehyde and acrolein.[1]

The following experiment made with crotonaldehyde and 0.1 per cent sodium hydroxide proves that it is slowly converted, at ordinary temperatures, into high-boiling and non-volatile red oils. Since acetaldehyde remains practically unchanged on similar treatment and aldol is converted very rapidly under these conditions, first into crotonaldehyde, etc., it is obviously impossible, by means of caustic alkalies, to convert aldehyde either into aldol or crotonaldehyde, as was also shown by special experiments described above.

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[1] Ann. Chem. (Liebig), **335**, 219.

In the first place it was proved that a mixture of 3.5 grams of crotonaldehyde and 3.5 grams of 0.1 per cent sodium hydroxide, when distilled directly, give back 2.7 grams of dry crotonaldehyde boiling at 98°–106°; in addition, 0.3 gram of nonvolatile, insoluble, red oil was obtained.

Five and three-tenths cc. of crotonaldehyde were now dissolved in 30 cc. of cold 0.1 per cent sodium hydroxide and the mixture was then allowed to stand in a closed vessel for 14 days at ordinary temperatures. On distillation 2.2 cc. of unchanged crotonaldehyde, which is 42 per cent of the amount taken, were recovered; in addition 0.3 gram of thick red oil, boiling at 90°–120° (30 mm.), and 1.3 grams of brown, nonvolatile resin were obtained from the alkaline solution by extraction with ether, etc.

On mixing equal volumes of aldol and 1 per cent sodium hydroxide in the cold, a noticeable rise of temperature is observed; the solution turns yellow, the odor of crotonaldehyde is very perceptible and soon an insoluble, yellowish oil separates out which gradually sinks and is transformed into a thick red oil. This oil, which is insoluble in water and freely soluble in ether, remains non-volatile when heated in a bath at 300° (20 mm.). Crotonaldehyde, on similar treatment, gives, apparently, the same red oil, which is obviously an intermediate product in the transformation of aldehyde, aldol, crotonaldehyde, etc., by caustic alkalies or concentrated sulphuric acid into aldehyde resin. The following experiments with aldol also show how readily this substance goes over into crotonaldehyde. A mixture of 6.4 grams of aldol, 14 cc. of water and 2 cc. of 0.1 per cent sodium hydroxide gave, after heating in a sealed tube at 100°, for 12 hours, no trace of acetaldehyde but 3.5 cc. of crotonaldehyde, or 71 per cent of the theory, and a total of 1.5 grams of high-boiling as well as non-volatile red oils.

Thirteen and three-tenths grams of aldol, b. p. 79° (20 mm.), and 50 cc. of water containing 1 gram of crystallized sodium acetate were heated in a sealed tube, for 20 hours, at 100°; no trace of acetaldehyde was formed, but 2.6 cc. of crotonaldehyde, boiling at 98°–106°, were obtained. The alkaline solution gave, on extracting with ether, etc., 5.8 grams of reddish oil which, on distillation (30 mm.), decomposed to a large extent, giving 1 cc. of yellowish, mobile oil, boiling at 100°–150° and leaving 1.6 grams of non-volatile red gum in the distilling flask.

A similar experiment, in which 13.9 grams of crotonaldehyde and 5 cc. of 28 per cent sodium acetate solution were heated in a sealed tube for 20 hours, at 100°, gave no trace of acetaldehyde but 6.4 cc. of unchanged crotonaldehyde and 4 grams of non-volatile reddish gum.

Six and five-tenths grams of aldol were dissolved, in the cold, in 70 cc. of water containing 0.5 gram of potassium carbonate. The solution became yellow and smelt strongly of crotonaldehyde. On working up in the usual manner, after 2 days' standing at ordinary temperatures, only a very small amount of crotonaldehyde and no trace of acetaldehyde was formed. The main product was a reddish, non-volatile gum, insoluble in water—obviously a condensation or polymerization product of crotonaldehyde.

A solution of 9.7 grams of aldol in 10 cc. of 1 per cent sulphuric acid was heated for 5 hours in a sealed tube, at 100°; 5.3 grams of thick brown oil had separated from the aqueous layer and was drawn off and distilled; 2 cc. of moist crotonaldehyde, boiling at 98°–106°, were obtained, but the main portion was a mixture of high-boiling as well as non-volatile red oils.

Similarly, 4 grams of aldol dissolved in 12 cc. of water containing 3 drops of 20 per cent sulphuric acid gave, after heating for 10 hours at 100°, in a sealed tube, no trace of aldehyde, 1.5 cc. of crotonaldehyde, 48 per cent of the theory, and a total of 1 gram of high-boiling and non-volatile reddish gum.

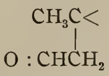
It is evident from the work of Nef that the function of the small amount of alkali or of sulphuric acid used in the experiments described above is to form temporarily with the aldol a salt,

$$CH_3CH(OM)CH_2CHO,$$

or an ester,

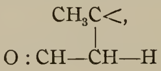
$$CH_3CH(OSO_2OH)CH_2CHO,$$

which, being *relatively more dissociated* into the alkylidene derivative,



$$\begin{array}{l} \quad CH_3C< \\ \qquad\ | \\ O:CHCH_2 \end{array} \quad \text{and} \quad HOM \quad \text{or} \quad H_2SO_4$$

than the mother substance, enables the intramolecular transformation of the methylene derivative,



$$\begin{array}{l} \qquad\qquad CH_3C<, \\ \qquad\qquad\quad | \\ O:CH—CH—H \end{array}$$

into crotonaldehyde

$$CH_3CH:CHCHO,$$

to take place *more rapidly* because of increased concentration.

On the Behavior of Acrolein and of Hydracrylic Aldehyde towards Alkalies.

A thorough investigation of the action of traces of mild and caustic alkalies on acrolein and on hydracrylic aldehyde was extremely desirable[1] and I therefore took up this study under Dr. Nef's guidance. The statement of Nef that these compounds are split under the conditions just named into crotonaldehyde, etc., was found to be incorrect. I have observed that all alkalies, both mild and caustic, when added in traces to a cold aqueous solution of acrolein invariably transform the substance quantitatively, and with marked evolution of heat, into an insoluble, amorphous polymer, which is perfectly analogous to the one obtained by Nef with acrolein and barium hydroxide. These polymers are neutral to sodium carbonate, but dissolve easily in 10 per cent sodium hydroxide and, after digesting for a short time at 100° and adding the calculated

[1] Ann. Chem. (Liebig), **335**, 220.

amount of hydrogen chloride, an amorphous, very high-melting substance is deposited whose weight is about one-half that of the polymer originally taken. The same end result is obtained with hydracrylic aldehyde and sodium hydroxide, although in this case no insoluble acrolein polymer is first deposited from the alkaline solutions on standing in the cold. These results made it impracticable to proceed further with the investigation and I therefore simply converted the remainder of my acrolein into hydracrylic aldehyde, in order to prove that this substance gives pentaerythrose, etc., when treated, in aqueous solution, with 2 mols. of formaldehyde, in the presence of traces of caustic alkali. All the acrolein used in my work was made from commercial glycerin and traces of phosphoric acid, according to Nef's directions.[1] I have found, after many trials, with 1 to 10 grams of phosphoric acid, that it is best to use 3 grams of phosphoric acid, sp. gr. 1.73, for every 100 grams of glycerin taken and to heat the mixture at first for 2.5 hours in a bath kept at 220°–240°, and then for one-half longer at 260°–300°. The yield of pure acrolein was regularly 10 grams for every 100 grams of glycerin taken, and the operation can be carried out successfully and without appreciable frothing by using 500 grams of glycerin at one time.

On the Acrolein Polymers.—Twenty-three and five-tenths grams of acrolein, b. p. 52°–58°, were dissolved in 184 cc. of water and 0.1 gram of potassium carbonate dissolved in 2 grams of water was then added in the cold. Turbidity sets in immediately and soon a large amount of a white substance separates out as a voluminous solid. The odor of acrolein was practically all gone after 18 hours' standing, but to insure complete transformation the mixture was treated with 0.1 gram more of potassium carbonate and allowed to stand 24 hours longer. Thus 22.5 grams of a white, amorphous substance, obviously, from its properties, polymeric acrolein were obtained. The polymer is insoluble in hot water, ligroin, ether, carbon bisulphide, benzene, glacial acetic acid; it dissolves easily in warm 95 per cent alcohol. On warming with dilute acids or alkalies, as well as on direct heating up to 100° and above, a strong odor of acrolein is at once noticed. My substance softened at 83° and decomposed, with gas evolution, at 94°–95°, whereas the perfectly analogous compound obtained by Nef[1] softens at 115° and decomposes at 128°–130°. It is quite possible that the polymers are space isomers, but as neither product could be obtained in the crystalline form the homogeneous nature of each is uncertain. Both dissolve, however, on warming in 10 per cent sodium hydroxide and give, apparently, the same end product.

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[1] Ann. Chem. (Liebig), **335**, 221, foot-note.

In repeating the experiment with 18.2 grams of acrolein, dissolved in 56 grams of water, it was observed that by an addition of 1 gram of potassium carbonate, dissolved in 4 cc. of water, a sudden and marked rise of temperature took place and that the transformation into the polymeric acrolein was practically complete in 15 minutes; 15 grams of amorphous substance, softening at 81° and decomposing at 94°–95°, were thus obtained.

Thirteen and eight-tenths grams of the polymeric acrolein were now heated in a distilling flask and the temperature of the surrounding bath was finally raised to 190°–220°; much tar formation took place and the distillate, 4.2 grams, gave, on fractionation, 2 cc. of acrolein boiling at 52°–60°.

As already mentioned, these polymers, as well as acrolein and hydracrylic aldehyde, all give red solutions on warming with 10 per cent sodium hydroxide; no crotonaldehyde nor its condensation products can have been formed in these cases for the solutions remain clear and give no aldehyde resin on long boiling.

After heating for 12 hours at 100° and then neutralizing with the calculated amount of hydrogen chloride, a light brown, flocculent precipitate is obtained. The weight in all cases was found to be about one-half of that of the substance taken. This precipitate is likewise amorphous, insoluble in water and practically all organic solvents and does not melt when heated up to 180°. It is neutral to sodium carbonate but dissolves easily and without change in sodium hydroxide.

[1] *Loc. cit.*

Pentaerythrose, $(CH_2OH)_3 \vdots CCH:O$*, from Mixtures of Formaldehyde and Acetaldehyde or Hydracrylic Aldehyde, Respectively.*

A solution containing 15 grams of aldehyde, 354 cc. of water and 87.6 grams of 35 per cent formaldehyde (3 mols.) was treated in the cold with 0.4 gram of powdered sodium hydroxide. No rise of temperature was noticed, but after 8 hours' standing the solution had become faintly acid; 0.4 gram more of sodium hydroxide was then added and, after standing over night, the same treatment was continued daily for 4 days, using, therefore, in all 3.2 grams of sodium hydroxide. The solution was now again faintly acid and the presence of formaldehyde could still be detected by a faint odor; the water was removed by distillation (25 mm.), heating, finally, on a boiling water-bath for 0.5 hour; 41.4 grams of thick, yellowish oil—crude pentaerythrose—remained in the distilling flask. A portion of the oil, 18.4 grams, was dissolved in 65.2 grams of acetic anhydride and then heated for 8.5 hours at 100°. The acylated gum, left after distilling off the acetic acid and anhydride (25 mm.), heating finally in a bath at 100°, was found to weigh 32.7 grams. It was freed from 4.53 grams of insoluble sodium salts by dissolving in 400 cc. of warm ether. The ethereal filtrate was then washed with 160 cc. of 10 per cent potassium carbonate and dried with calcium chloride. The ether was distilled off and the last traces present removed by heating at 100° (20 mm.); 27 grams of a yellowish, mobile oil remained, which is evidently acylated pentaerythrose, containing also some acylated pentaerythrite and acetylated β,β'-dihydroxyisobutyric aldehyde. The oil is insoluble or very sparingly soluble in water and all attempts to convert it into the solid state were fruitless. On distillation (30 mm.) 5.3 grams of the oil gave, with marked decomposition, 3.2 grams of distillate boiling at 215°–230°. Furthermore, the acylated oil, on treatment with phenylhydrazine, gave no well-defined derivative; the only thing left to do was to convert the oil back into pentaerythrose by hydrolysis with water. This was done by heating to 100° 3 times with 5 parts of water in periods of 10 hours each and distilling off the water and acetic acid after each operation under 20 mm., heating, finally, on a boiling water-bath. Twenty-nine and nine-tenths grams of acylated oil gave thus 17.8 grams, 16.1 grams and, finally, 15.5 grams of crude pentaerythrose as a highly viscous, yellowish oil. The oil is very soluble in cold water and alcohol, reduces Fehling's solution on warming, but all attempts to convert it into the solid state or into a crystalline derivative have, up to the present time, resulted in failure. That much pentaerythrose is present is proved, however, by the fact that the oil gives, on reduction with sodium amalgam in dilute acid solution,[1] a fair amount of pentaerythrite,[2] melting at 253°. For this purpose the crude pentaerythrose, obtained directly from the aqueous solution after condensation and subsequent removal of the water, was used; it contained, therefore, some sodium formate; 18.4 grams of gum were dissolved in 62.5 grams of water and treated, in the course of 6 hours, with 2.5 per cent sodium amalgam containing 9.3 grams of sodium, 1.5 times the theory, taking care to keep the solution at about 0° and faintly acid throughout the operation by continual addition of dilute sulphuric acid.

The water was then distilled off from the neutralized solution (20 mm.) and the salt residue, 67.5 grams, digested with 300 cc. of absolute alcohol, leaving 52.7 grams of insoluble salts. On cooling, the alcoholic filtrate gave 2.65 grams of pentaerythrite and on removing the alcohol entirely 9.6 grams of crystalline residue remained. The latter gave, on crystallization from a very small amount of water, 1.2 grams of a crystalline substance which melted at 170°–180°. The 12.25 grams of material soluble in the hot alcohol were finally resolved, by repeated fractional crystallization from water and alcohol, mainly into 2 products besides some unchanged pentaerythrose gum; namely, 3.2 grams melting at 220°–253°, from which 2.2 grams of practically pure pentaerythrite, m. p. 248°–253°, were obtained and 2.7 grams of substance melting between 170°–180°. It is extremely probable that this lower melting substance, which was also noticed by Tollens and Rave[1] in their work, is trihydroxytrimethylmethane,

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[1] E. Fisher: Ber. d. chem. Ges., **23**, 3685.

[2] Tollens and Wigand: Ann. Chem. (Liebig), **265**, 322.

$$(CH_2OH)_3 \vdots CH.$$

The analytical data given by Tollens and Rave, in fact, agree very well with those demanded by this compound. It must, therefore, be inferred that the crude pentaerythrose obtained in my experiments contains fairly large amounts of β,β'-dihydroxyisobutyric aldehyde.

The following experiment with hydracrylic aldehyde and 2 mols. of formaldehyde proves that in this case also large amounts of pentaerythrose[2] are formed:

Nineteen and six-tenths grams of hydracrylic aldehyde, made according to Nef's directions,[3] but not distilled and simply freed from water and acrolein by heating in a bath at 80° (20 mm.), were dissolved in 78.4 grams of water; 45.4 grams of 35 per cent formaldehyde and, thereupon, 14 cc. of 1 per cent sodium hydroxide were added in the cold. A rise of 5° in temperature was noticed during the following 30 minutes and after 24 hours the solution had become neutral to litmus; 0.14 gram more of sodium hydroxide was now added daily for 13 days, or a total of 1.96 grams in all.

The aqueous solution, which was practically neutral and had still a faint odor of formaldehyde, was now freed from water by distillation (20 mm.), heating finally in a bath at 100° for 0.5 hour; 35 grams of crude pentaerythrose gum, containing some sodium formate, were thus obtained. The gum was dissolved in 107 grams of acetic anhydride[4] and heated at 100° for 9 hours; after getting rid of the acetic acid and anhydride by distillation (25 mm.) on a boiling water-bath, 58.9 grams of acylated gum were obtained. This was freed from 5.66 grams of sodium salts by dissolving in 300 cc. of warm ether. On distilling off the ether and removing the last traces by heating for 2 hours in a bath at 100° (18 mm.), 49.35 grams of a mobile, reddish acylated oil, insoluble in water, were obtained—obviously acylated pentaerythrose containing small amounts of acetylated pentaerythrite and β,β'-dihydroxyisobutyl aldehyde.

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[1] Ann. Chem. (Liebig), **276**, 59, foot-note.

[2] Cf. Klüger: Monats. Chem., **26**, 885.

[3] Ann. Chem. (Liebig), **335**, 219.

[4] Special experiments with hydracrylic aldehyde and acetic anhydride have proved that at 100° no acetyl derivative but a non-volatile, at 300° (20 mm.), condensation product is formed.

Hydrolysis of the Acylated Oil.—The 49.35 grams of oil were now hydrolyzed by heating with 5 parts of water at 100°, for 10 hours, repeating the operation 3 times and removing the acetic acid, etc., formed by distillation (25–30 mm.) in a bath at 100°. The amount of non-volatile gum left after each treatment was 34 grams, 31.9 grams, and finally, 30.5 grams. The last portion obviously now consists mainly of pentaerythrose and shows a behavior which is in every way analogous to that shown by the crude pentaerythrose obtained from formaldehyde and acetaldehyde. It is a reddish, viscous gum, quite soluble in cold water and alcohol and reduces Fehling's solution on warming. Up to the present time all attempts to obtain a crystalline derivative, or to solidify the oil, have failed. The investigation of pentaerythrose will be continued in the near future. I wish especially to study also its oxidation products and to convert the crude pentaerythrose from hydracrylic aldehyde into pentaerythrite and trihydroxytrimethylmethane by means of sodium amalgam, in acid solution.

On the Action of Aqueous Copper Acetate on the Hexoses.

In view of the experimental difficulties presenting themselves in connection with the study of crude pentaerythrose and because of my desire to complete my studies during the present academic year, Dr. Nef suggested that I assist him in his study of the action of oxidizing agents on the sugars—a problem to which he has been devoting himself for over 2 years past.[1] The task assigned to me was the quantitative determination of the amount of cuprous oxide, carbon dioxide, formic, glycollic and oxalic acids formed from 100 grams of *d*-glucose, *d*-fructose and *d*-galactose by 8 hours' heating on a boiling water-bath with an excess, 10 mols., of aqueous copper acetate. Preliminary experiments by Nef, carried out in the autumn of 1904, had established the formation of the acids named except formic acid, and their relative amounts had, also in part, been ascertained by him. My own quantitative results confirm his observations in these particulars. The other acids formed in the oxidation with copper acetate, which give calcium salts very soluble in water and precipitated by alcohol and which constitute about 40 per cent of the total reaction products, are at present being investigated by Nef; it is obviously impossible to present a theory of the oxidation of hexoses until this work is completed.

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[1] Ann. Chem. (Liebig), **335**, 323–333.

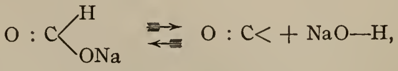
d-Glucose and Copper Acetate.—Twenty grams of *d*-glucose, m. p. 140°–150°, dissolved in 50 grams of water, were added to a warm solution of 225 grams of crystallized copper acetate, $Cu(C_2H_3O_2)_2.H_2O$, 10 mols., in 2 liters of water. The mixture was heated for 8 hours on a boiling water-bath under a reversed condenser. This operation was repeated 5 times, and in all 99 grams of dextrose were taken. The amount of carbon dioxide given off with 10 grams of dextrose and a corresponding amount of aqueous copper acetate was determined in a special experiment, as follows: The mixture was heated for 8 hours on a boiling water-bath, during which period a steady stream of carbon dioxide-free air was passed through the solution and the gaseous products were drawn through 2 tall cylinders filled with saturated barium hydroxide solution; 5.46 grams of barium carbonate, well washed and dried at 100°, were obtained, which corresponds to 12.2 grams of carbon dioxide from 100 grams of dextrose. Nef obtained, in a similar experiment with 20 grams of dextrose, etc., after heating for 6 hours in an oil-bath at 100°–110°—at the higher temperature the reaction is more complete—13.2 grams of barium carbonate, corresponding to 14.75 grams of carbon dioxide from 100 grams of dextrose. It was noticed that most of the carbon dioxide, as well as the greater part of the cuprous oxide, is formed during the first hour's heating.

Nef obtained, in his experiment with 20 grams of dextrose, 64 grams of cuprous oxide, whereas the average amount obtained by me in 4 experiments was 59.6 grams for every 20 grams of *d*-glucose. It was proved by special experiments—by dissolving in hydrogen chloride, precipitating with hydrogen sulphide, etc.—that the cuprous oxide obtained was, in all cases, practically free from cupric or cuprous oxalate. From these data the amount of oxygen taken up in the oxidation of *d*-glucose was 4.08 atoms in my experiments.

The aqueous filtrates from the cuprous oxide were now united, the copper still present in large amounts was precipitated by hydrogen sulphide and the filtrate freed from hydrogen sulphide by drawing air through the hot solutions under a reversed condenser. The water was then distilled off slowly under reduced pressure until the volume of the solution reached about 2 liters, whereupon small amounts of sulphuric acid, formed by the oxidation of the copper and hydrogen sulphides, were removed by digestion with small portions of barium hydroxide so that, finally, the solution contained traces of barium. The water in the aqueous filtrate was now removed by distillation (20 mm.) and to insure complete removal of the volatile fatty acids present the residual gum was again dissolved in water and the distillation, under reduced pressure, repeated, heating, finally, on a boiling water-bath for 0.5 hour.

As an end result, 99 grams of dextrose gave 63.5 grams of non-volatile gum and 17.185 liters of distillate, containing water, acetic and formic acids.

The amount of formic acid present in the distillate was determined quantitatively by H. C. Jones' method[1] with potassium permanganate—a method which depends upon the fact that acetic acid is not oxidized in sodium carbonate solution at 70°–80° with 0.1 N potassium permanganate, whereas, sodium formate, being relatively much dissociated according to



$$\mathrm{O : C}{<}\begin{matrix}\mathrm{H}\\ \mathrm{ONa}\end{matrix} \rightleftarrows \mathrm{O : C}{<} + \mathrm{NaO{-}H},$$

is oxidized quantitatively to carbon dioxide under these conditions.

Preliminary experiments with much acetic acid and known quantities of formic acid proved that the method is perfectly reliable; the results obtained, however, with the above-mentioned aqueous distillate are not absolutely final concerning the amount of formic acid present because the aqueous distillates, in the case of all hexoses used, were found to reduce Fehling's solution very slightly on vigorous boiling. This shows that some volatile sugar must be present, but I was unable to determine whether the product was formaldehyde or glycollic aldehyde; obviously, however, some of the permanganate must be used up in oxidizing this substance. Furthermore, it was ascertained by special experiment that the copper acetate used in all my work contained the following amount of reducible material: Copper acetate, 20 grams, were digested for 2 hours with 100 cc. of water, 100 cc. of saturated sodium carbonate solution and with 20 cc. of 10 per cent. sodium hydroxide and the solution was then filtered from the insoluble black copper oxide. The colorless filtrate was acidified and made up to 1 liter; 100 cc. of this solution were then made alkaline with sodium carbonate and treated with an excess of 0.1 N potassium permanganate at 70°–80°, for 0.5 hour; the solution was then acidified with sulphuric acid, treated with an excess of 0.1 N oxalic acid and titrated back with 0.1 N potassium permanganate. It was found thus that 12.52 cc. 0.1 N potassium permanganate are used up in oxidizing the impurities present in 20 grams of copper acetate; a corresponding correction, was, therefore, introduced, depending upon the amount of copper used in my oxidation experiments.

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[1] This Journal, **17**, 539. Cf. Lieben: Monats. Chem., **14**, 146. Peau de St. Gilles: Ann. de chim. et d. Phys., (3), **55**, 388.

Thus the amount of formic acid present in the aqueous distillate, 17.185 liters, obtained from 99 grams of dextrose, was found to be 9.93 grams, as follows: One hundred cc. of the distillate were treated with sodium carbonate and an excess of 0.1 N potassium permanganate, at 70°–80°, for 0.5 hour; the solution was then acidified with dilute sulphuric acid, treated with an excess of 0.1 N oxalic acid and titrated back with 0.1 N potassium permanganate; 29.06 cc. of 0.1 N potassium permanganate were used up in this oxidation. Deducting the amount of permanganate necessary for the oxidation of the copper acetate used with 99 grams dextrose, we find that a total of 4317.6 cc. of 0.1 N potassium permanganate is necessary for the oxidation of the formic acid. This corresponds, therefore, to 10.03 grams of formic acid for every 100 grams of dextrose taken.

Determination of the Oxalic and Glycollic Acid in the Non-volatile Gum.

The 63.5 grams of non-volatile acid gum obtained from dextrose was dissolved in hot water and digested for 2 hours with an excess, 64 grams, of powdered calcium carbonate. The 50.04 grams of insoluble calcium salts which were thus obtained were proved, by digestion with 100 cc. of water and 150 cc. of 30 per cent acetic acid, to consist of unchanged calcium carbonate and of 14.5 grams of calcium oxalate, corresponding to 8.9 grams of anhydrous oxalic acid.

0.2829 gram substance, dried at 100°–120°, gave, on ignition, 0.1081 gram CaO.

	Calculated for $CaC_2O_4.H_2O$.	Found.
Ca	27.45	27.29

The aqueous filtrate containing the soluble calcium salts and unchanged sugars was now concentrated, under reduced pressure, to a small volume and the calcium salts then precipitated by the addition of much alcohol. The salts which came down at first in a gummy state gradually get solid on rubbing with a pestle. The calcium salts still left in the aqueous alcoholic filtrate were then removed by further concentration and subsequent precipitation by alcohol. Thus a total of 46.8 grams of brown calcium salts was obtained. The quantity of calcium present, determined by ignition of a portion with sulphuric acid, was found to be 11.6 per cent. On dissolving the lime salts in a very small quantity of hot water a total of 5.57 grams of calcium glycollate, in 3 fractions, separated out on long standing. This corresponds to 3.25 grams of free glycollic acid and an analysis of the last 2 fractions, crystallized once more from water, gave the following result:

1.2161 grams substance, dried at 100°–120°, lost 0.3441 gram H_2O.

0.3086 gram of dry salt gave, on ignition, 0.0910 gram CaO.

	Calculated for $Ca(C_2H_3O_3)_2.4H_2O$.	Found.
H_2O	27.48	28.29
CaO	29.47	29.49

It is extremely probable that some calcium glycollate was still held in solution by the more soluble lime salts present, consequently my determinations of the amount of glycollic acid formed from the sugars are probably low both in the case of dextrose and of levulose.

On precipitating the lime in the aqueous filtrate from the 5.57 grams of calcium glycollate mentioned above, with the calculated amount of oxalic acid and then distilling off the water (20 mm.), heating, finally, in a bath up to 100°, 29 grams of gummy acids remained. These were converted, by digestion with 3 parts of acetic anhyhride at 100°, for 9 hours, etc., into 43.5 grams of acylated gum; only 26.2 grams of the gum dissolved on digestion with ether and the remainder, 17.3 grams of dark brown gum, gave, on threefold hydrolysis with 5 parts of water at 100°, 10.5 grams of dark brown acid tar.

The aqueous alcoholic filtrates obtained after the second precipitation of lime salts by alcohol were now concentrated to a small volume; it was proved by the addition of alcohol that only traces of lime salts are present. The amount of neutral, nonvolatile gum present in the solution was, therefore, determined by distillation under reduced pressure, heating, finally, to 100°; 20.3 grams brown gum were thus obtained. It was shown, by titration with Fehling's solution, to contain 8.68 grams of dextrose, leaving, therefore, 11.62 grams of material undetermined. The presence of unchanged dextrose in the gum was established by the fact that a portion of the gum, when treated in the cold with aqueous phenylhydrazine acetate, gave a fair amount of the osazone of *d*-glucosone, m. p. 205°.

Finally, it should be mentioned that a special experiment with 9 grams of *d*-glucose and the corresponding amount of aqueous copper acetate was carried out in the usual manner, in which the absence of carbonic oxide, or of any other gaseous product except carbon dioxide, was established beyond a doubt.

Levulose and Copper Acetate.—One hundred grams of *d*-fructose, m. p. 102°–105°, were treated, in portions of 20 grams each, with aqueous copper acetate (10 mols.) for 8 hours in a boiling water-bath. The average amount of cuprous oxide obtained was 68.2 grams for every 20 grams of fruit sugar taken, whereas Nef obtained, in 1904, from a similar amount after 5.5 hours' heating in an oil- bath at 100°–110°, 71.5 grams of cuprous oxide. These results show that more oxygen is taken up in the burning of levulose than in that of dextrose. The difference must, however, be attributed in part to the fact that less unchanged sugar is found at the end of the experiment in the case of *d*-fructose, 2.9 per cent as compared with 8.8 per cent in the case of dextrose.

The amount of carbon dioxide formed was also found to be noticeably larger in this case, for 10 grams fruit sugar gave, on heating for 8 hours in a boiling water-bath with aqueous copper acetate, 7.25 grams of barium carbonate, which corresponds to 16.17 grams of carbon dioxide from 100 grams of levulose.

On removing the excess of copper in the combined filtrates from 100 grams of levulose by hydrogen sulphide, etc., 64.4 grams of non-volatile and very dark-colored gum remained in the distilling flask. This gave, on treatment with hot water, 10.25 grams of insoluble tar, and digestion of the aqueous filtrate with 80 grams powdered calcium carbonate, etc., gave 63.07 grams of insoluble calcium salts, which were proved to consist of unchanged calcium carbonate and of 10.65 grams of calcium oxalate, corresponding to 6.56 grams of anhydrous oxalic acid. The aqueous filtrate, containing the soluble calcium salts, gave, on concentration to about 100 cc. and after standing for 1 week, 7.68 grams of crude calcium glycollate; and this, on crystallization from 50 cc. of water, gave 3.4 grams of pure calcium glycollate in snow-white, bulky needles.

3.3817 grams substance, dried at 100°–120°, lost 0.917 gram H_2O.

0.2532 gram dried salt gave, on ignition, 0.0748 gram CaO.

	Calculated for $Ca(C_2H_3O_3)_2.4H_2O$.	Found.
H_2O	27.40	27.10
CaO	29.47	29.54

The aqueous filtrate from the 7.68 grams of crude calcium glycollate gave, on concentration and precipitation by alcohol, 48 grams of light-brown calcium salts which, on analysis, were found to contain 14.54 per cent of calcium; these gave, when digested with the calculated amount of oxalic acid, etc., 34.8 grams of non-volatile acid gums which were resolved by digestion with 500 cc. of ethyl acetate (6 times) and then with 5 parts of absolute alcohol (2 times) into 18.7 grams of gum soluble in ethyl acetate, 8.4 grams soluble in alcohol and 7.7 grams of dark-brown, tarry acid gum insoluble in these solvents.

In order to determine the amount of formic acid formed in the oxidation a duplicate experiment, carried out with 50 grams of levulose, gave the following result; the total aqueous distillate was found to require 3149.6 cc. of 0.1 N potassium permanganate for the oxidation of the formic acid, after making the usual corrections as stated above. From these data the amount of formic acid formed in the oxidation of 100 grams of levulose is found to be 14.50 grams. The non-volatile portion gave, on treatment with water, an excess of powdered calcium carbonate, etc., 4.89 grams of calcium oxalate, dried at 100°, corresponding to 3.01 grams of anhydrous oxalic acid.

0.3496 gram substance gave, on ignition, 0.1337 gram CaO.

	Calculated for $CaC_2O_4.H_2O$.	Found.
Ca	27.45	27.31

The aqueous filtrate containing the soluble calcium salts was concentrated to a small volume and the salts present precipitated by alcohol, in the usual manner. On digesting these with the calculated amount of oxalic acid, etc., 26.1 grams of brown, gummy acids were obtained. These gave, when digested successively with ethyl acetate and absolute alcohol, as above in the first levulose experiment, 12.5 grams of gum, soluble in ethyl acetate, 8.1 grams of gum soluble in alcohol and 5.5 grams of dark-brown insoluble acid tar.

On working up the aqueous alcoholic filtrates from the precipitated soluble calcium salts, by distillation under reduced pressure, heating, finally, in a bath at 100°, only 3.5 grams of gum, practically free from calcium salts, were obtained; this was proved by titration with Fehling's solution, to contain 1.46 grams of unchanged levulose. Furthermore, an aqueous solution of the gum gave, on standing with aqueous phenylhydrazine acetate, the osazone of *d*-glucosone, m. p. 199°–202°. The experiment shows, therefore, that decidedly less unchanged sugar (2.9 per cent) remains in the case of levulose than in that of *d*-glucose (8.8 per cent) and *d*-galactose (8.5 per cent).

Copper Acetate and d-Galactose.—The amount of oxygen taken up and of carbon dioxide formed in the oxidation of *d*-galactose by aqueous copper acetate is noticeably less than in the case of fruit or grape sugar.

Fifty grams of *d*-galactose, m. p. 152°–154°, were treated in 3 portions with aqueous copper acetate, 8 hours, at 100°, in the usual manner. The average amount of cuprous oxide obtained fom 20 grams of *d*-galactose was only 55.3 grams and Nef obtained, in 2 experiments in 1904, an average of 58 grams on heating for 6 hours in an oil-bath at 100°–110°.

The amount of carbon dioxide obtained from 10 grams of *d*-galactose and the corresponding amount of aqueous copper acetate was only 0.463 gram (2.1 grams of barium carbonate) after 8 hours' heating on a boiling water-bath.

Titration of the aqueous distillate with potassium permanganate, in the usual manner, showed that a total of 2347.4 cc. of 0.1 N solution was necessary for the oxidation of the formic acid present. These data prove that 100 grams of *d*-galactose give 11 grams of formic acid. Forty-two and eight-tenths grams of non-volatile, gummy acids were obtained; these gave, on digestion with 40 grams of powdered calcium carbonate, etc., 36.2 grams of insoluble lime salts, containing, as shown by heating with dilute acetic acid, 9.38 grams of calcium oxalate, dried at 100°, and corresponding to 5.78 grams of anhydrous oxalic acid.

0.2321 gram substance gave, on ignition, 0.0892 gram CaO.

	Calculated for $CaC_2O_4.H_2O$.	Found.
Ca	27.45	27.45

In addition to this 0.72 gram of copper oxalate separated out from one galactose portion on standing, *i. e.*, before precipitating the copper in the filtrate from the cuprous oxide by hydrogen sulphide; therefore the amount of anhydrous oxalic acid obtained from 50 grams of *d*-galactose was 6.16 grams.

The aqueous filtrate from the insoluble calcium salts gave, on concentration and addition of alcohol, 29 grams of lime salts, dried at 80°–90°; these were found, by titration with Fehling's solution, to contain 1.19 grams of *d*-galactose, but the amount of calcium glycollate present was not determined in this case. Finally, the aqueous alcoholic filtrates from the precipitated lime salts were found, on distillation under reduced pressure, to contain 11.5 grams of gum; this material contained 3.06 grams of unchanged *d*-galactose, as determined by titration with Fehling's solution. Therefore, the total amount of unaffected galactose amounted to 4.25 grams or 8.5 per cent. The presence of this sugar was also established by treating a portion of the gum with aqueous phenylhydrazine acetate in the cold; on standing, a large amount of an osazone melting at 190° was obtained.

The Action of Aqueous Copper Acetate on Formaldehyde, Formic, Glycollic and Oxalic Acids.

The following experiments with aqueous copper acetate and the reagents named are of importance; first, they prove that the formic and carbonic acids obtained in the oxidation of the hexoses cannot possibly be attributed to the breaking down of a portion of the oxalic acid formed as an intermediate product; second, because they prove that the oxalic acid obtained cannot possibly come from an oxidation of glycollic acid; third, because they show, very decisively, that the carbon dioxide obtained from the hexoses cannot possibly come, to any appreciable extent, from an oxidation of formic acid:

(*a*) One hundred and twelve and five-tenths grams of copper acetate, dissolved in a liter of water containing 10 grams of formic acid (sp. gr. 1.22), were heated in a boiling water-bath for 6.5 hours under a reversed condenser. During the entire period a slow stream of air, free from carbon dioxide, was drawn steadily through the solution and then through 2 tall cylinders filled with saturated barium hydroxide solution. A very small amount of carbon dioxide is slowly and steadily evolved, although no precipitation of cuprous oxide could be detected. Only 0.89 gram of barium carbonate, or 0.2 gram of carbon dioxide, was obtained.

(*b*) A similar experiment with 112.5 grams of copper acetate, 1 liter of water and 29 grams of 35 per cent formaldehyde gave, after heating in an air current for 6.5 hours on a boiling water-bath, no trace of barium carbonate, as shown by an absence of even turbidity in the cylinders containing the barium hydroxide.

(*c*) A mixture of 28 grams of copper acetate, 2 grams of glycollic acid, 2 grams of acetic acid and 1 liter of water was heated in a boiling water-bath for 6 hours in a manner entirely similar to (*a*) and (*b*), but no trace of cuprous oxide or carbon dioxide could be found.

(*d*) Two and five-tenths grams of crystallized oxalic acid, dissolved in water, were added to a warm solution of 28 grams of copper acetate, 25 grams of acetic acid and 900 grams of water. The oxalic acid is precipitated at once and completely as white cupric oxalate, and this is invariably the case, no matter what proportion of acetic acid is present. The mixture was now heated on a boiling water-bath for 8 hours under practically the same conditions as were employed in (*a*), (*b*) and (*c*); no change took place and no trace of carbon dioxide was evolved during this period.

This result is in marked contrast to that obtained with aqueous copper acetate and the 3 hexoses, where the oxalic acid found in the oxidation experiments remained entirely in the solution, *i. e.*, did not come down as cupric oxalate either with the cuprous oxide or subsequently from the filtrate which still contained much copper acetate even on long standing. It is, therefore, not improbable that the oxalic acid actually obtained from the hexoses, as stated above, may have been formed by the subsequent hydrolysis of an unknown intermediate product.

In conclusion, I wish to express a deep feeling of appreciation of the help and encouragement which Dr. Nef has given me in the whole course of this work.

ACYL DERIVATIVES OF ORTHO- AND PARAMINOPHENOL.

By J. Bishop Tingle and L. F. Williams.

In the course of some other work which is now in progress in this laboratory we desired to carry out a series of experiments with ortho- and paraminophenol and with a considerable number of their mono- and diacyl derivatives. We have found that the recorded methods of preparing some of these compounds are not always consistent with each other and that in certain cases it was advisable to modify a published procedure in order to obtain a good yield; moreover, the properties of several of our products differ from those given in the literature; for these reasons, and also because we have synthesized a number of acyl derivatives which have not hitherto been described, we have decided to publish our results in the present paper, without waiting for the completion of the main part of our research.

The first step in our work was the conversion of ortho- and paranitrophenol into the corresponding monacetylaminophenols. Of the methods which have been suggested for this purpose that of Morse,[1] which consists in reducing the nitrophenols by means of acetic acid and tin, appeared to be the most convenient, but Zincke and Hebebrand[2] state that it failed to give them the desired compounds. Professor Morse informs us that he has received, in private communications, similar statements from other chemists, but that in the hands of some workers the method has given complete satisfaction. He suggested that these conflicting experiences might be accounted for by variation in the concentration of the acetic acid which was employed and that the best results would be obtained by the use of absolutely anhydrous acetic acid. Accordingly, we titrated some of the best glacial acetic acid obtainable and added to it recently distilled acetic anhydride, in quantity exactly sufficient to raise the acid content to 100 per cent. By means of this mixture and by carefully excluding moisture from the apparatus, we experienced no difficulty in obtaining a yield of each monacetylaminophenol equal to 50 per cent of the theoretical.

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[1] Ber. d. chem. Ges., **11**, 232.

[2] Ann. Chem. (Liebig), **226**, 69.

By adding concentrated hydrochloric acid in excess, to the crude solution of acetylorthoaminophenol, which is obtained after removal of the tin and evaporating the mixture to dryness, orthoaminophenol hydrochloride is readily formed.

From acetylorthoaminophenol, m. p. 201°, we prepared the following derivative, by the Schotten-Baumann method:

Dibenzoylorthoaminophenol, $C_6H_5CO\overset{1}{O}C_6H_4\overset{2}{N}HCOC_6H_5$, crystallizes from alcohol in slender, white needles, melting at 180°. Its formation in this manner has not been previously recorded; it involves replacement of both acetyl and hydrogen by benzoyl groups.

The preparation of paranitrobenzoyl derivatives was effected by gradually mixing paranitrobenzoyl chloride, dissolved in benzene, with an aqueous solution of orthoaminophenol hydrochloride and adding, at intervals, small quantities of 20 per cent potassium hydroxide solution. The experiment was conducted in an atmosphere of carbon dioxide because free aminophenol is extremely sensitive to oxygen, especially in the presence of alkali. Operating under these conditions, we obtained 2 compounds, which were separated by means of acetone.

Paranitrobenzoylorthoaminophenol,
$H\overset{1}{O}C_6H_4\overset{2}{N}H\overset{1}{C}OC_6H_4\overset{4}{N}O_2$, is deposited from alcohol in small, yellow crystals melting at 220°. It is tolerably readily soluble in acetone.

Diparanitrobenzoylorthoaminophenol,
$O_2\overset{4}{N}C_6H_4\overset{1}{C}O\overset{1}{O}C_6H_4\overset{2}{N}H\overset{1}{C}OC_6H_4\overset{4}{N}O_2$, is practically insoluble in the ordinary organic media. It crystallizes from nitrobenzene in slightly gray, feathery crystals, melting at 219°.

The corresponding metanitrobenzoyl derivatives were obtained in a similar manner to the para compounds.

Metanitrobenzoylorthoaminophenol,
$H\overset{1}{O}C_6H_4\overset{2}{N}H\overset{1}{C}OC_6H_4\overset{3}{N}O_2$, is insoluble in benzene, but readily dissolves in hot acetone, from which it is deposited in small, yellow crystals, melting at 206°.

Dimetanitrobenzoylorthoaminophenol, $O_2\overset{3}{N}C_6H_4\overset{1}{C}OO\overset{1}{C}_6H_4\overset{2}{N}H\overset{1}{C}OC_6H_4\overset{3}{N}O_2$, easily dissolves in benzene at the ordinary temperature and crystallizes from alcohol in light, flaky plates, which melt at 188°.

Under the same conditions as were employed in the case of paranitrobenzoyl chloride, except that the potassium hydroxide solution was only 10 per cent, phenylsulphonic chloride and orthoaminophenol hydrochloride yielded *phenylsulphoneorthoaminophenol*, $H\overset{1}{O}C_6H_4\overset{2}{N}HSO_2C_6H_5$. It was deposited from benzene or ether in small needles, which were almost white and melted at 141°. In another experiment carried out under similar conditions as nearly as they could be reproduced, except that we used a different preparation of phenylsulphonic chloride, we obtained only *diphenylsulphoneorthoaminophenol*, $C_6H_5SO_2\overset{1}{O}C_6H_4\overset{2}{N}HSO_2C_6H_5$, which was deposited from alcohol in slightly reddish columnar crystals melting at 134°. Georgesco states[1] that he obtained only diphenylsulphoneorthoaminophenol, m. p. 81°–83°, from phenylsulphonic chloride and orthoaminophenol, by the Schotten-Baumann reaction, but, in spite of several attempts, we were unable to prepare a compound with this melting point, or to detect its presence in our product. We regret that Georgesco's original paper is not accessible to us.

The formation of acetylparaminophenol from paranitrophenol was effected in the same manner as in the case of the ortho compound. Here, likewise, absolute acetic acid must be employed and moisture excluded from the apparatus. Under these conditions the preparation presents no special difficulties.

We also obtained the compound by the action of tin amalgam on the nitrophenol, in the presence of acetic acid of 100 per cent concentration. The experiments were carried out in an apparatus of special construction,[2] lent to us by Professor Morse. By means of an electric current the amalgam is produced continuously in the apparatus and various mechanical devices en-sure constant contact between fresh amalgam and the nitro compound.

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[1] **Chem. Centrabl., 1900, I., 543. Buletinul. Societatii de Scinte, 8, 668.**

[2] *Vide* **H. P. Straus: Dissertation, Johns Hopkins University, 1905.**

Acetylparaminophenol behaves towards concentrated hydrochloric acid like the ortho compound. It melts at 166°. The melting point, 179°, given by Morse,[1] is due to a printer's error. In the course of some experiments with this compound we heated it on the water-bath with alcohol, 95 per cent, and camphoroxalic acid. The product, after purification by means of ethyl acetate, strongly resembled the original acetaminophenol in its appearance, but melted at 170° instead of 166°. Closely agreeing analyses showed the content of carbon to be 0.5 per cent too high and that of nitrogen 0.9 per cent too low, *vide* p. 65. By heating at 105° the compound lost in weight to the extent of 0.43 per cent and then showed the same composition as at first and also, practically, the original melting point, 166°.5. Such behavior in this substance does not appear to have been observed before. We believe that it can be best explained as follows: A portion of the acetyl derivative is hydrolyzed by the water in the alcohol, under the catalytic influence of the camphoroxalic acid, and the mixture, or solid solution of acetyl derivative and aminophenol combines with some ethyl acetate. As this latter is not present in the crystals in any simple molecular ratio, it is probably to be regarded more as a solid solution than as ethyl acetate of crystallization. During the heating process acetylation once more takes place, by the action of free acetic acid present in the ethyl acetate and so, in this way and by the elimination of ethyl acetate, the original substance is regenerated.

By the action of acetyl chloride we obtained the diacetyl derivative, $CH_3CO\overset{1}{O}C_6H_4\overset{4}{N}HCOCH_3$, m. p. 150°, which has been described by Ladenburg,[2] whose method of preparation was much less convenient.

Benzoyl chloride reacts with acetylparaminophenol under the conditions of the Schotten-Baumann method, yielding *N-Acetyl-O-benzoylparaminophenol,*

$$C_6H_5CO\overset{1}{O}C_6H_4\overset{4}{N}HCOCH_3,$$

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[1] Ber. d. chem. Ges., 11, 232.

[2] *Ibid.*, 9, 1529.

which is deposited from alcohol in white, feathery crystals melting at 166°.5. This difference in the action of benzoyl chloride on the ortho and paracetylaminophenols is interesting and suggestive (*vide* p. 52).

While this paper was in the hands of the printer, Reverdin[1] published a description of O-acetyl-N-benzoylparaminophenol and of O-benzoyl-N-acetylparaminophenol. Both compounds are stated to melt at 171°. Our melting points were determined with care and the purity of our compound is shown by analysis. Reverdin's experimental conditions differed somewhat from those employed by us and his analytical results comprise merely one nitrogen determination. We can only explain the difference in melting point by supposing that possibly his compound contained some monobenzoyl derivative. The coincidence in the melting point of his 2 substances is striking and suggestive.

Albert W. Smith, who prepared benzoylparaminophenol by the action of phosphorus pentachloride on *syn*-hydroxybenzophenoneoxime and also from benzoyl chloride and paraminophenol, gives the melting point as 205°–207°.[2] Our substance, also made from benzoyl chloride, melted at 227°.5.

When paranitrobenzoyl chloride is allowed to react with paraminophenol hydrochloride, under conditions similar to those described for the ortho compound (p. 52), two substances are formed: *Paranitrobenzoylparaminophenol*,

$$H\overset{1}{O}C_6H_4\overset{4}{N}H\overset{1}{C}OC_6H_4\overset{4}{N}O_2,$$

is deposited upon alcohol in small, glistening, orange-red, monoclinic crystals, melting at 258°. *Diparanitrobenzoylparaminophenol*,

$$O_2\overset{4}{N}C_6H_4\overset{1}{C}O\overset{1}{O}C_6H_4\overset{4}{N}H\overset{1}{C}OC_6H_4\overset{4}{N}O_2,$$

is obtained from solution in nitrobenzene in light yellow, microscopic crystals, melting at 264°.

Metanitrobenzoyl chloride also yields 2 compounds: *Metanitrobenzoylparaminophenol*, $H\overset{1}{O}C_6H_4\overset{4}{N}H\overset{1}{C}OC_6H_4\overset{3}{N}O_3$, which crystallizes from acetone in slender, light yellow needles, melting at 215°–216°. *Dimetanitrobenzoylparaminophenol,*

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[1] Ber. d. chem. Ges., 39, 3794 (1906).

[2] *Ibid.*, 24, 4042 (1891).

$$O_2\overset{3}{N}C_6H_4\overset{1}{C}O\overset{1}{O}C_6H_4\overset{4}{N}H\overset{1}{C}OC_6H_4\overset{3}{N}O_2,$$

is deposited from nitrobenzene as a light gray powder, melting at 264°–265°.

The action of phenylsulphonic chloride on paranitrophenol was studied under conditions similar to those employed with orthoaminophenol. Under these circumstances we obtained only *phenylsulphoneparaminophenol,* $H\overset{1}{O}C_6H_4\overset{4}{N}HSO_2C_6H_5$, which crystallizes from benzene in slender, slightly colored needles, melting at 156°.5 Georgesco[1] states that he obtained this compound and also diphenylsulphoneparaminophenol,

$$C_6H_5SO_2\overset{1}{O}C_6H_4\overset{4}{N}HSO_2C_6H_5,$$

and gives the melting point of the former as 125°–126° and of the latter as 150°–152°. We have repeated our experiments several times and, in the absence of details regarding the conditions which he used, we can only suggest, as the probable cause of the discrepancy between his results and ours, that he failed to purify his substances; this would explain why our *mono*-sulphone melts more than 4° higher than his *di*-sulphone. The analytical figures for our compound are given in the second part of the present paper. It may also be pointed out, in support of the correctness of our results, that they agree in every way with those reported by Troeger and Uhlmann[2] for the paratolylsulphones. They also obtained only monosulphones of ortho- and paraminophenol. Moreover, their ortho compound melts at 138°–139°, a little below the para derivative, which melts at 143°; the melting points of our compounds, 141° and 156°.5, respectively, correspond closely to these and show the same relationship. For convenience of comparison and by way of a summary, we show in the following table the simpler mono- and diacyl derivatives of ortho and paraminophenol. We have tried to make the list complete. The figures represent the melting points of the respective compounds. Those described for the first time in this paper are given in *italics*. It will be noticed that out of a total of 30 substances included in the table, 12 have been prepared for the first time by us; of the remaining 18 we have prepared 2 by a new, simpler method, have shown that the existence of 2 is decidedly doubtful and have corrected the melting point of another one:

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[1] *Loc. cit.*

[2] J. prakt. Chem. [2], **51**, 438, 441 (1895).

Table Showing the Simpler Acyl Derivatives of Ortho- and Paraminophenol.

	Orthoaminophenol.		Paraminophenol.	
Name of acid radical.	Monacyl derivative.	Diacyl derivative.	Monacyl derivative.	Diacyl derivative.
Acetyl	201°	123°–124°	166°	*150°*[1]
Acetyl-benzoyl				*166°.5*
Acetyl-ethylsulphonyl				136°
Acetyl-picryl				165°
Acryl	123°–124°			
Benzoyl	167°	*180°*[1]	*227°.5*[2]	233°–234°
Benzoyl-acetyl				171°
Chloracetyl	136°			
Metanitrobenzoyl	*206°*	*188°*	*215°–216°*	*264°–265°*
Methylsulphonyl			89°–90°	
Paranitrobenzoyl	*220°*	*219°*	*258°*	*264°*
Paratolylsulphonyl	138°–139°		143°	
Phenylsulphonyl	*141°*	81°–83°[3]	*156°.5*	150°–152°[3]
Picryl		*134°*	174°	

A number of experiments at 0°, at the ordinary temperature and at 240°–250° have been made in order to obtain tribenzoyl derivatives of ortho- and paraminophenols. In every case without success.

EXPERIMENTAL.

Preparation of Orthoacetoaminophenol.—Orthonitrophenol (12 grams, 1 mol.) was mixed in a capacious, round-bottomed flask with glacial acetic acid, 50 grams = 10.5 mol., to which sufficient recently distilled acetic anhydride had been added to bring the acid content to 100 per cent. The flask was attached to a long reversed condenser, suitably protected from the moisture of the atmosphere and the contents of the flask were heated until the nitrophenol had dissolved. To this solution granulated tin, 15 grams, was added. The reduction commenced immediately and the action quickly became very vigorous. It is desirable to allow the reaction to proceed as rapidly as is possible without loss of substance. As soon as the action moderates, a second portion of tin, 15 grams, is added and, if necessary, external heat is applied to bring practically all of the metal into solution. The liquid is now poured into 2 liters of water, the mixture warmed and a current of hydrogen sulphide passed into it until no further precipitate of stannous sulphide takes place. Sometimes it is convenient to filter the liquid through cheese cloth before all the tin has been thrown down and then, later, to make a final filtration through paper.

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[1] Prepared by new method.

[2] Previous melting point corrected.

[3] Existence doubtful.

The clear filtrate is concentrated until crystals appear; after being cooled the crystals are drained and recrystallized twice fom 95 per cent alcohol. The compound melts at 201°, as stated by Morse[1] and by Ladenburg.[1] This yield is 40–45 per cent of the theoretical.

Preparation of Orthoaminophenol Hydrochloride.—This compound is readily obtained by adding an equal volume of concentrated hydrochloric acid to the clear filtrate from the stannous sulphide and then evaporating to a small bulk. Should this concentrated liquid have the odor of acetic acid, more hydrochloric acid is added and the heating repeated until all acetic acid has been expelled. The hydrochloride readily forms crystals and may be purified by recrystallizing twice from water, with the addition of a little animal charcoal. It has no melting point within the range of our thermometers. The yield is about 50 per cent of the theoretical.

Action of Benzoyl Chloride on Orthoacetaminophenol. — The acetaminophenol, 14 grams = 1 mol., was dissolved in warm water and mixed with benzoyl chloride, 20 grams = $1\frac{2}{3}$ mol. The liquids were well shaken and to them was added, in small portions, sufficient aqueous solution of potassium hydroxide, 10 per cent, to produce a permanent alkaline reaction. A precipitate which formed, finally, was removed, washed with water and recrystallized from alcohol. It is deposited in slender white needles, which melt at 180° and were found to consist of *dibenzoylorthoaminophenol.* The yield was excellent.

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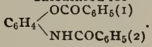
[1] *Loc. cit.*

Analysis:

I. 0.1455 gram substance gave 0.4032 gram CO_2 and 0.0674 gram H_2O.

II. 0.1822 gram substance gave 7.7 cc. N at 22° and 760 mm.

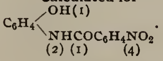
	Calculated for	Found.	
	 $C_6H_4{<}\begin{array}{l}OCOC_6H_5(1)\\NHCOC_6H_5(2)\end{array}.$	I.	II.
C	75.7	75.57	. .
H	4.73	5.14	. .
N	4.41	. .	4.65

Action of Paranitrobenzoyl Chloride on Orthoaminophenol Hydrochloride.—Free orthoaminophenol is readily colored by oxygen, consequently, experiments which involve the action of an alkali on the aminophenol hydrochloride were always carried out in an atmosphere of carbon dioxide. Paranitrobenzoyl chloride being a solid, it was found to be most convenient to employ it in benzene solution.

The aminophenol hydrochloride, 5 grams = 1 mol., was dissolved in water and mixed with a benzene solution of paranitrobenzoyl chloride, 12.7 grams = 2 mols. Potassium hydroxide, 20 per cent aqueous solution, was added gradually, the mixture being constantly shaken; this was continued until the liquid became permanently alkaline. The precipitate which formed was removed and, after being washed with water and dried, it was placed in a Soxhlet apparatus and extracted with acetone. The portion which dissolved was recrystallized from alcohol. It formed slightly yellow, light, feathery crystals, melting at 220°.

Analysis:

0.1677 gram substance gave 16.2 cc. N at 23°.5 and 764 mm.

	Calculated for	Found.
	 $C_6H_4{<}\begin{array}{l}OH(1)\\ \underset{(2)}{NH}\underset{(1)}{CO}C_6H_4\underset{(4)}{NO_2}\end{array}.$	
N	10.85	10.9

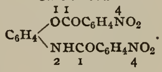
These results show that the body is *paranitrobenzoylorthoaminophenol.*

The compound that was insoluble in acetone was recrystallized from nitrobenzene; the deposited crystals, which were light and feathery, were washed with benzene. They melted at 219°. The substance, which proved to be *diparanitrobenzoylorthoaminophenol,* is practically insoluble in water, ethyl and methyl alcohols, ether, chloroform, ethyl acetate, benzene, toluene and ligroin.

Analysis:

I. 0.1495 gram substance gave 0.3214 gram CO_2 and 0.0443 gram H_2O.

II. 0.1409 gram substance gave 13 cc. N at 20° and 750 mm.

	Calculated for	Found.	
	 $C_6H_4\left<\begin{matrix}\overset{1\;1}{OC}OC_6H_4\overset{4}{N}O_2 \\ \underset{2}{N}H\underset{1}{C}OC_6H_4\underset{4}{N}O_2\end{matrix}\right.$.	I.	II.
C	58.96	58.63	. .
H	3.19	3.29	. .
N	10.31	. .	10.4

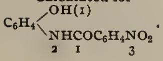
The total yield of these 2 compounds was 80–90 per cent of the theoretical, in the ratio of 3 parts mono- : 5 parts of the dinitrobenzoyl derivative.

Action of Metanitrobenzoyl Chloride on Orthoaminophenol Hydrochloride.—The experiments with these compounds were carried out under exactly the same conditions as those with paranitrobenzoyl chloride which are described above. We worked with 10 grams (1 mol.) of the hydrochloride and 21.4 grams (1.7 mol.) of the acid chloride. The product of the reaction was extracted with benzene in a Soxhlet apparatus. The residue, insoluble in benzene, was dissolved in acetone, from which it separated in small, yellowish crystals, which melted at 206° and were found to consist of *metanitrobenzoylorthoaminophenol.*

Analysis:

I. 0.1541 gram substance gave 0.3434 gram CO_2 and 0.0600 gram H_2O.

II. 0.1108 gram substance gave 10.6 cc. N at 24° and 758 mm.

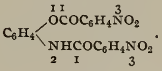
	Calculated for	Found.	
	 $C_6H_4\left\langle\begin{matrix}OH(1)\\ \underset{2}{N}H\underset{1}{C}OC_6H_4\underset{3}{N}O_2\end{matrix}\right.$.	I.	II.
C	60.46	60.77	. .
H	3.87	4.32	. .
N	10.85	. .	10.69

The second product of the reaction, which was soluble in benzene, was purified by solution in alcohol, from which it was deposited in light, feathery crystals with a slight pinkish tinge. It melted at 186° and proved to be *dimetanitrobenzoylorthoaminophenol.*

Analysis:

I. 0.1165 gram substance gave 0.2504 gram CO_2 and 0.0418 gram H_2O.

II. 0.1307 gram substance gave 12.2 cc. N at 23° and 759 mm.

	Calculated for	Found.	
	 $C_6H_4\left\langle\begin{matrix}\overset{1}{O}\overset{1}{C}OC_6H_4\overset{3}{N}O_2\\ \underset{2}{N}H\underset{1}{C}OC_6H_4\underset{3}{N}O_2\end{matrix}\right.$.	I.	II.
C	58.96	58.61	. .
H	3.19	3.98	. .
N	10.31	. .	10.5

The total yield of these 2 compounds was about 80–90 per cent of the theoretical, of which rather more than half consisted of the dinitrobenzoyl derivative.

Action of Phenylsulphonic Chloride on Orthoaminophenol Hydrochloride.—These experiments were carried out under similar conditions to those employed in the case of paranitrobenzoyl chloride, *vide* p. 59. It was, of course, unnecessary to use benzene. We took 5 grams (1 mol.) of the hydrochloride and 12 grams (2 mols.) of the sulphonic chloride in each experiment; the concentration of the potassium hydroxide solution was 10 per cent. The crude, solid product of the reaction was dried and extracted with benzene in a Soxhlet apparatus, to remove a small quantity of tarry matter. After evaporation of the benzene the material which had dissolved in it was recrystallized from ether, being deposited in slender, pale-pink crystals, which are readily soluble in alcohol and melt at 141°.

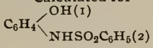
It proved to be *phenylsulphoneorthoaminophenol.* The yield of purified product was about 70 per cent of the theoretical.

Analysis:

I. 0.1101 gram substance gave 0.2346 gram CO_2 and 0.0469 gram H_2O.

II. 0.1347 gram substance gave 6.8 cc. N at 24°.5 and 763 mm.

III. 0.2302 gram substance gave 0.2216 gram $BaSO_4$.

	Calculated for  $C_6H_4\left\langle\begin{array}{l}OH(1)\\NHSO_2C_6H_5(2)\end{array}\right.$	Found.		
		I.	II.	III.
C	57.83	58.14	. .	. .
H	4.41	4.73	. .	. .
N	5.5	. .	5.51	. .
S	12.88	. .		13.22

In another series of experiments in which we used 2.9 grams (1 mol.) of orthoaminophenol hydrochloride and 4 grams of phenylsulphonic chloride (1.25 mol.) with 10 per cent potassium hydroxide, the other conditions being as nearly as possible identical with those described above, we obtained only *diphenylsulphoneorthoaminophenol.* In other experiments in which the proportions of reacting substances were exactly the same as those used in the preparation of the monosulphone we again obtained merely the disubstituted compound. The only cause of this difference in behavior, which we have been able to detect, is in the phenylsulphonic chloride, two samples of which were at our disposal. Both of these were in Kahlbaum's original packages, but one always gave us the mono- and the other the disubstituted compound. This latter substance crystallizes from alcohol in reddish rods which melt at 134°.

Analysis:

I. 0.1476 gram substance gave 0.2939 gram CO_2 and 0.0582 gram H_2O.

II. 0.2029 gram substance gave 6.5 cc. N at 24° and 751 mm.

III. 0.2174 gram substance gave 0.2548 gram barium sulphate.

IV. 0.1532 gram substance gave 0.1786 gram barium sulphate.

	Calculated for $C_6H_4<^{OSO_2C_6H_5\ (1)}_{NHSO_2C_6H_5\ (2)}$.	Found.			
		I.	II.	III.	IV.
C	55.49	55.23	. .	. .	. .
H	3.85	4.38	. .	. .	. .
N	3.59	. .	3.46	. .	. .
S	16.47	. .	. .	16.10	16.01

We are indebted to Mr. Nirdlinger, of this laboratory, for Analysis IV.

A number of experiments were also made with a third sample of phenylsulphonic chloride which was likewise one of Kahlbaum's preparations. It had been in stock for some time before we used it. With orthoaminophenol hydrochloride and this compound we obtained what appeared to be mixtures of the mono- and disulphones, melting at 126°.8. The monosulphone melts at 141° and the disubstituted compound at 134°. Mixtures of the two melt at 118° and a mixture of monosulphone and of the third preparation mentioned above (m. p. 126°.8) melts at 121°.

The discrepancy between our results and those of Georgesco has already been pointed out, *vide* p. 53. We made several attempts to prepare his diphenylsulphone derivative by varying the experimental conditions and the proportion of phenylsulphonic chloride, but without success. The low melting-point of Georgesco's disulphone, 81°–83°, and its red color, make us very doubtful as to the purity of his substance.

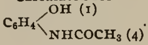
Preparation of Paracetoaminophenol.—This compound was prepared from paranitrophenol exactly in the same manner as the ortho derivative (p. 57). A few experiments were made for us by Dr. C. W. Gray to determine whether it was advantageous to prepare paracetoaminophenol by the electrolytic reduction of paranitrophenol in acetic acid solution. As will be apparent from what follows, the ordinary meaning of the term "electrolytic reduction" is hardly applicable to the conditions under which we worked; the active reducing agent was tin amalgam, which was continuously produced under the influence of the electric current. Paranitrophenol, 9 grams, and acetic acid of 100 per cent concentration, 35 grams, were placed in the cathode vessel. A rod of pure tin was inserted into the anode compartment. The 2 vessels were connected by means of mercury and the whole apparatus was mounted on a wooden stand, to which could be imparted an automatic, steady rocking motion. This apparatus was designed by Professor Morse and is practically identical with that fully described and illustrated by H. P. Strauss,[1] who worked under his direction. By the use of a graphite-coated, electric furnace, constructed according to the description of Morse and Frazer,[2] the cathode compartment could be heated to any desired temperature.

The reduction of the nitrophenol proceeded without difficulty under these conditions, and the product of the reaction was worked up in the same manner as that obtained by the use of acetic acid and granulated tin. The yield was about 40 per cent of the theoretical.

This acetyl derivative was purified by solution in water, from which it is deposited in colorless, well-formed, monoclinic crystals. These melt at 166°, as given by Friedlander.[3] Because of the varying statements in the literature regarding the melting point of this compound, it was further identified by analysis.

I. 0.1891 gram substance gave 0.4403 gram CO_2 and 0.1019 gram H_2O.

II. 0.2104 gram substance gave 17.8 cc. N at 20° and 767 mm.

	Calculated for	Found.	
	 $C_6H_4{<}\begin{smallmatrix}OH\ (1)\\ NHCOCH_3\ (4)\end{smallmatrix}$.	I.	II.
C	63.57	63.44	. .
H	5.96	5.98	. .
N	9.27	. .	9.6

The yield was about 47 per cent of the theoretical.

In the course of some experiments with this substance we had occasion to heat it on the water-bath with a solution of camphoroxalic acid in 95 per cent alcohol. A crystalline product was obtained which closely resembled paracetaminophenol, but melted at 170°.

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[1] Dissertation, Johns Hopkins University, 1905.

[2] THIS JOURNAL, 32, 93 (1904).

[3] *Loc. cit.*

Analysis:

I. 0.1343 gram substance gave 0.3150 gram CO_2 and 0.0716 gram H_2O.

II. 0.1429 gram substance gave 0.3357 gram CO_2 and 0.0766 gram H_2O.

III. 0.2843 gram substance gave 21.5 cc. N at 22°.5 and 760 mm.

IV. 0.1765 gram substance gave 13.3 cc. N at 21°.5 and 755 mm.

	Calculated for		Found.			
	$C_6H_4\langle^{OH(1)}_{NHCOCH_3(4)}$.	$C_6H_4\langle^{OH(1)}_{NH_2(4)}$.	I.	II.	III.	IV.
C	63.57	66.05	64.09	64.07	. .	. .
H	5.96	6.42	5.92	5.95	. .	. .
N	9.27	12.84	. .	. .	8.35	8.32

A portion of the compound was heated at 105° until its weight became constant. The loss in weight amounted to 0.43 per cent. After this heating the substance melted at 166°.5, instead of 170° and, when analyzed, proved to be paracetaminophenol.

Analysis:

I. 0.1346 gram substance gave 0.3138 gram CO_2 and 0.0742 gram H_2O.

II. 0.2101 gram substance gave 17.5 cc. N at 20° and 752 mm.

	Calculated for	Found.	
	$C_6H_4\langle^{OH(1)}_{NHCOCH_3(4)}$.	I.	II.
C	63.57	63.58	. .
H	5.96	6.12	. .
N	9.27	. .	9.24

As stated more fully in the theoretical portion of this paper, we believe that the changes described above are due to the hydrolysis of a portion of the acetaminophenol; this would raise the carbon content; the percentage of nitrogen would, however, be reduced on account of the ethyl acetate which was retained, whereas this would produce much less effect on the carbon and hydrogen values. During the heating to drive off this ethyl acetate, acetylation of the hydrolyzed product took place, so that, finally, we obtained acetaminophenol regenerated in a state of purity.

Preparation of Paraminophenol Hydrochloride.—This salt is readily prepared by adding to the clear filtrate from the stannous sulphide precipitate an equal volume of concentrated hydrochloric acid and evaporating to dryness. Should acetic acid be present towards the completion of the evaporation, more hydrochloric acid must be added and the heating continued. The product is purified by recrystallizing once or twice from water in the presence of a little animal charcoal. The yield of purified substance is about 45–50 per cent of the theoretical.

Action of Acetyl Chloride on Paracetaminophenol. — When these compounds are mixed, in equimolecular proportions, and gently heated, they quickly react. The product was crystallized from water. It melted at 150° and corresponded, in general properties, with the substance prepared by Ladenburg[1] from paraminophenol and acetic anhydride. The yield was practically quantitative.

Action of Benzoyl Chloride on Paracetaminophenol. — The experiments with these compounds were carried out under similar conditions to those employed in the case of orthoaminophenol. We worked in aqueous solution and used 10 per cent potassium hydroxide. The chloride and the acetaminophenol were employed in equimolecular proportion. The product of the reaction separated as a solid; after being washed it was recrystallized from alcohol, from which it was deposited in white, feathery crystals, melting at 166°.5. It is sparingly soluble in hot water but practically insolubie in cold. The compound proved to be *N-acetyl-O-benzoylparaminophenol.* The yield was about 90 per cent of the theoretical.

Analysis:

I. 0.1699 gram substance gave 0.4392 gram CO_2 and 0.0787 gram H_2O.

II. 0.1017 gram substance gave 5 cc. N at 19°.5 and 752 mm.

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[1] Ber. d. chem. Ges., 9, 1529 (1876).

	Calculated for $C_6H_4\left<\begin{matrix}OCOC_6H_5\ (1)\\ NHCOCH_3\ (4)\end{matrix}\right.$.	Found.	
		I.	II.
C	70.58	70.44	. .
H	5.09	5.14	. .
N	5.49	. .	5.58

Action of Paranitrobenzoylchloride on Paraminophenol Hydrochloride.—These substances were allowed to react under conditions similar to those employed in the case of orthoaminophenol. The quantities taken were 5 grams (1 mol.) of the hydrochloride and 16 grams (2.5 mol.) of the acid chloride. The solid product was washed with water, dried and extracted in a Soxhlet apparatus with acetone. The greater portion remained undissolved. The substance soluble in acetone did not dissolve at all readily in ethyl alcohol, but it was deposited from methyl alcohol in small, orange-red crystals, melting at 258°. It also dissolves in ethyl acetate. We obtained the same compound, as the only product of the reaction, by intimately mixing finely divided paraminophenol hydrochloride, 3 grams (1 mol.), with the acid chloride, 4.2 grams (1.1 mol.), and heating in an open vessel at 160°. The resulting material was triturated in a mortar with 10 per cent sodium carbonate solution and then recrystallized from alcohol. The compound proved to be *paranitrobenzoylparaminophenol.*

Analysis:

I. 0.1384 gram substance gave 0.3067 gram CO_2 and 0.0548 gram H_2O.

II. 0.1852 gram substance gave 18.1 cc. N at 23°.5 and 770 mm.

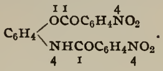
	Calculated for $C_6H_4\left<\begin{matrix}\overset{1}{OH}\\ \underset{4}{N}H\underset{1}{CO}C_6H_4\underset{4}{NO_2}\end{matrix}\right.$.	Found.	
		I.	II.
C	60.46	60.43	. .
H	3.87	4.39	. .
N	10.85	. .	10.85

That portion of the product of the Schotten-Baumann reaction which was insoluble in acetone was crystallized from nitrobenzene; it formed a light yellow powder, melting at 264°. It did not dissolve in water, ethyl alcohol, ether, methyl alcohol, ethyl acetate, nor in hot or cold aqueous potassium hydroxide solution. The substance proved to be *diparanitrobenzoylparaminophenol.*

Analysis:

I. 0.1067 gram substance gave 0.2312 gram CO_2 and 0.0343 gram H_2O.

II. 0.2285 gram substance gave 21 cc. N at 21° and 751 mm.

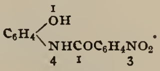
	Calculated for	Found.	
	 $C_6H_4\left<\begin{matrix}\overset{1}{O}\overset{1}{C}OC_6H_4\overset{4}{N}O_2\\ \underset{4}{N}H\underset{1}{C}OC_6H_4\underset{4}{N}O_2\end{matrix}\right.$.	I.	II.
C	58.96	59.09	. .
H	3.19	3.57	. .
N	10.31	. .	10.12

The total yield of these compounds was about 80–90 per cent of the theoretical, in the proportion of approximately 3 parts of the mono- : 5 parts of the diacyl derivative.

Action of Metanitrobenzoyl Chloride on Paraminophenol Hydrochloride.—The hydrochloride, 5 grams (1 mol.), in aqueous solution, was mixed with the acid chloride, 12.8 grams (2 mols.), dissolved in benzene, and aqueous potassium hydroxide, 20 per cent solution, was added. The conditions of the experiment were exactly like those described for paranitrobenzoyl chloride and orthoaminophenol hydrochloride, *vide* p. 59. The solid product of the reaction, after being washed with water and dried, was extracted in a Soxhlet apparatus with ethyl acetate. The portion which dissolved in this solvent crystallized from acetone in slender, light yellow needles, melting at 215°–216°. It was sparingly soluble in alcohol and proved to be *metanitrobenzoylparaminophenol.*

Analysis:

0.1612 gram substance gave 0.3588 gram CO_2 and 0.0627 gram H_2O.

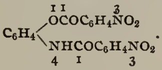
	Calculated for	Found.
	 $C_6H_4\left<\begin{matrix}\overset{1}{O}H\\ \underset{4}{N}H\underset{1}{C}OC_6H_4\underset{3}{N}O_2\end{matrix}\right.$.	
C	60.46	60.70
H	3.87	4.32

That portion of the reaction product which did not dissolve in ethyl acetate was purified by solution in nitrobenzene, from which it was deposited as a gray powder, melting at 264°–265°. It was insoluble in all the ordinary organic media and consisted of *dimetanitrobenzoylparaminophenol.*

Analysis:

I. 0.1764 gram substance gave 0.3824 gram CO_2 and 0.0599 gram H_2O.

II. 0.2342 gram substance gave 22.6 cc. N at 26° and 760 mm.

	Calculated for  $\mathrm{C_6H_4}\left<\begin{matrix}\overset{1}{\mathrm{O}}\overset{1}{\mathrm{C}}\mathrm{OC_6H_4}\overset{3}{\mathrm{N}}\mathrm{O_2} \\ \underset{4}{\mathrm{N}}\mathrm{H}\underset{1}{\mathrm{C}}\mathrm{OC_6H_4}\underset{3}{\mathrm{N}}\mathrm{O_2}\end{matrix}\right.$.	Found. I.	 II
C	58.96	59.12	. .
H	3.19	3.77	. .
N	10.31	. .	10.39

The total yield of these 2 compounds was 80–90 per cent of the theoretical, in the ratio of about 1 part mono-: 2 parts of dimetanitrobenzoyl derivative.

Action of Phenylsulphonic Chloride on Paraminophenol Hydrochloride.—The work with these substances was carried out exactly as in the case of the corresponding experiments with orthoaminophenol, *vide* p. 61. The quantities employed were 5 grams (1 mol.) of the hydrochloride and 12 grams (2 mols.) of the acid chloride. The solid product of the reaction was treated with benzene; a small portion of insoluble tarry matter remained. The part which dissolved was crystallized from ether and deposited in slender, white needles, melting at 156.5. It is readily soluble in alcohol, and consisted entirely of *phenylsulphoneparaminophenol* irrespective of which of the three samples of sulphonic chloride was employed, *vide* p. 62. An experiment was made with a different proportion of sulphonic chloride but the product was identical with the one first obtained.

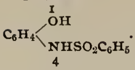
Analysis:

I. 0.1201 gram substance gave 0.2555 gram CO_2 and 0.0542 gram H_2O.

II. 0.1624 gram substance gave 8.3 cc. N at 27° and 758 mm.

III. 0.2301 gram substance gave 0.2189 gram $BaSO_4$.

IV. 0.2202 gram substance gave 0.2086 gram $BaSO_4$.

	Calculated for  $C_6H_4\langle{}^{1}OH,\ {}^{4}NHSO_2C_6H_5$.	Found. I.	 II.	 III.	 IV.
C	57.85	58.01	. .	. .	. .
H	4.41	5.01	. .	. .	. .
N	5.5	. .	5.45	. .	
S	12.88	. .	. .	12.01	13.01

Analysis IV was made for us by Mr. Nirdlinger, of this laboratory.

The yield was 70–80 per cent of the theoretical.

All our efforts to prepare a diphenylsulphone were unsuccessful.

Mr. Marshall P. Cram has been good enough to carry out for us a number of experiments with the object of obtaining *triacyl derivatives* of ortho and paraminophenol. As they have, unfortunately, not been attended with success they will be described very briefly. Orthoaminophenol hydrochloride, 7.25 grams (1 mol.), and benzoyl chloride, 50 grams (7 mol.), were mixed and treated with potassium hydroxide, 23 grams (8 mol.), in 15 per cent aqueous solution. The mixture was allowed to remain at the ordinary temperature for 3 weeks. In a second experiment, similar to the above, the materials were allowed to remain for 3 weeks, at 0°. Two further experiments were made at the ordinary temperature and at 0°, respectively, using pyridine, 100 cc., instead of the potassium hydroxide. Finally, all 4 experiments were repeated with paraminophenol hydrochloride instead of the ortho compound. The products from the experiments with potassium hydroxide were poured into water, filtered, and recrystallized from benzene. Only the dibenzoylaminophenols were obtained. From the aqueous filtrate benzoic acid alone could be isolated. The product from the pyridine experiments was extracted with ether, washed with water and the residue crystallized from benzene; it proved to be the dibenzoyl compound. The ethereal solution was extracted with dilute sulphuric acid and then evaporated; the residue was a mixture of benzoic and monobenzoylaminophenol.

Experiments were next tried at a high temperature. Dibenzoylparaminophenol, 72 grams, was mixed with dehydrated sodium benzoate, 2.7 grams, 1 drop of concentrated sulphuric acid and a large excess of benzoyl chloride, 11.4 grams, and heated in a sealed tube for 1.5 working days, at 240°. A portion which was removed and tested showed that no reaction had taken place, consequently the heating was continued for another day, at 250°. This treatment caused incipient decomposition. Only the unchanged disubstitution derivative could be obtained from the product. A similar experiment was made with dibenzoylorthoaminophenol, but the conditions of heating were 1.5 days, at 240°. The result was similar to that obtained with the para compound.

JOHNS HOPKINS UNIVERSITY,
June, 1906.

ON THE SALTS OF TAUTOMERIC COMPOUNDS.

[EIGHTH COMMUNICATION ON URAZOLES.]

Preliminary Paper.

BY S. F. ACREE.

For several years the writer has been investigating[1] the reactions of some tautomeric substances and their salts, especially in the urazole series,[2] with the hope of securing more light on the behavior of these interesting and peculiar substances. The work on the reactions of the salts of some tautomeric substances has reached the point where a preliminary notice is desirable. The investigations will be continued in this laboratory and a more detailed account of the results will be published later. This paper deals only with the metallic salts of tautomeric compounds which are acids, and work on the acid salts of tautomeric substances which are bases will be published later.

The urazoles contain amide groups and exist in solutions in the following states of equilibrium: C, C^{I}, etc. represent the concentrations and K, K^{I}, etc., the equilibrium constants.

$$(1)\quad \underset{C}{\overset{+}{H}} + \underset{C^{I}}{\overset{-}{N}\mathrm{(R)COR}} \underset{K}{\rightleftarrows} \underset{C^{II}}{\mathrm{HN(R)COR}} \underset{K^{II}}{\rightleftarrows}$$

---

[1] The writer is indebted to the Carnegie Institution of Washington for aid in this work.

[2] THIS JOURNAL, **27**, 118; **31**, 185; **32**, 606. Ber. d. chem. Ges., **35**, 553; **36**, 3139; **37**, 184, 618.

$$\underset{C^{III}}{RN : C(OH)R} \underset{K^{I}}{\rightleftarrows} \underset{C^{IV}}{RN : C(R)\overset{-}{O}} + \underset{C}{\overset{+}{H}}.$$

Mr. G. H. Shadinger has proved that the values of C, C^{I}, etc. K, K^{I}, K^{II}, etc., vary greatly with the individual urazoles and with the conditions of solution. When such a system is treated with a sodium hydroxide solution the following states of equilibrium[1] are formed according to the laws governing (1) and (2).

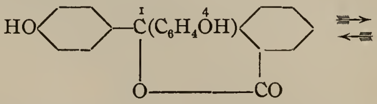
$$(2)\ \underset{C_{1}}{\overset{+}{Na}} + \underset{C_{1}^{I}}{\overset{-}{N}(R)COR} \underset{K_{1}}{\rightleftarrows} \underset{C_{1}^{II}}{NaN(R)COR} \underset{K_{1}^{II}}{\rightleftarrows}$$

$$RN : \underset{C_{1}^{III}}{C(R)ONa} \underset{K_{1}^{I}}{\rightleftarrows} RN : \underset{C_{1}^{IV}}{C(R)\overset{-}{O}} + \underset{C_{1}}{\overset{+}{Na}}.$$

It has been proved experimentally that equilibrium exists between C^{II} and C^{III} in (1) and between C_{1}^{II} and C_{1}^{III} in (2), and that $K^{II} = \frac{C^{II}}{C^{III}}$ and $K_{1}^{II} = \frac{C_{1}^{II}}{C_{1}^{III}}$. It therefore follows that K_{1}, K_{1}^{I}, and K_{1}^{II} may vary greatly with different salts prepared from (1) and (2), a conclusion entirely justified by experiment. It further follows that even when K or K^{I} in (1) is very small, or zero, K_{1} or K_{1}^{I} in (2) may be comparatively large.

These relations probably hold for other tautomeric substances, such as ethyl acetoacetate types, nitrophenols, nitrosophenoles, phenolphthalein types, etc. In some cases, however, it may be found that the equilibrium is wholly between the ions.

Julius Stieglitz[2] and others believe that in substances of the phenolphthalein type the equilibrium may be expressed by the equations:

(3)


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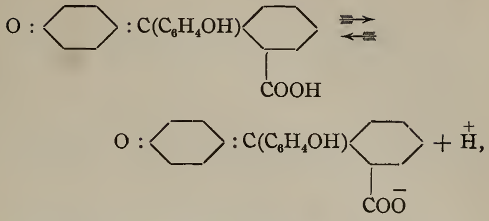
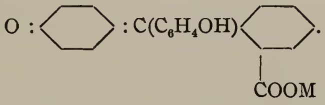
[1] Baly, Marsden and Stewart: J. Chem. Soc., 89, 966. Hantzsch and Ley: Ber. d. chem. Ges., 39, 3149.

[2] J. Am. Chem. Soc., 25, 1119.



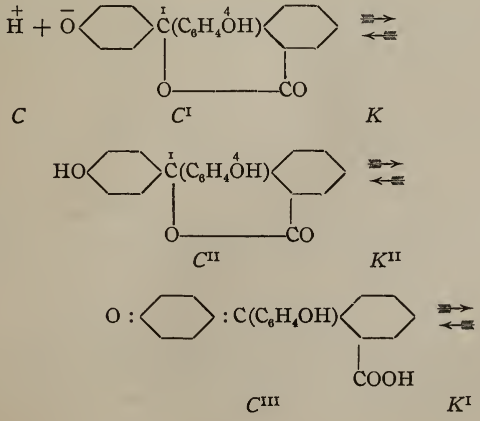
and that the simple salts have the constitution

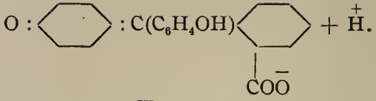


They see in such an assumption the explanations of the color changes in indicators of this type.

The writer feels, however, that such an explanation is inadequate and that the following equations are more in harmony with the known facts:

(4)

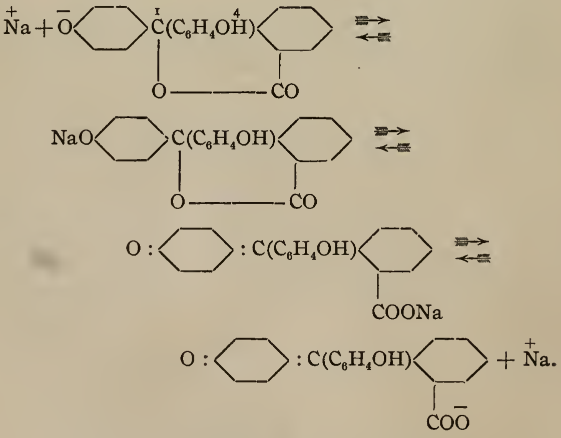




C^{IV} C

Furthermore, the other phenol group is probably ionized to a very small extent. Since the affinity constant for benzoic acid,[1] for example, is $K = 0.00006$ and that of phenol[2] is $K = 0.0000005$, and further, since C^{II} is undoubtedly much larger than C^{III} (phenolphthalein is not colored in solution) it follows that the value of C^{I} and the hydrogen ions corresponding must be considerable in comparison with C^{IV}. The reasoning employed above with the urazoles leads at once to the conclusion that the following set of equations express the equilibrium conditions present in solutions of the salts prepared by treating (4) with sodium hydroxide.

(5)



Such an explanation not only makes clear the color changes involved in the use of such indicators, but also the formation of the various phenol and carboxyl derivatives when the salts[1] of fluorescein, for example, are treated with alkyl halides.

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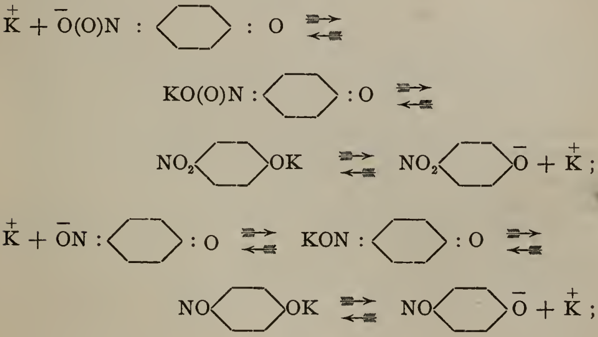
[1] Z. physik. Chem., 3, 418.

[2] Hantzsch; Ber. d. chem. Ges., 32, 3066.

Work in this laboratory on the alkylation of the salts of nitro and nitrosophenols, and of ethyl acetoacetate types, leads the writer to believe, contrary to the views of Nef,[2] Michael,[3] and Claisen[4] that the salts of these substances exist in solution in a condition that may be fairly represented in the following equations:[5]



$$\overset{+}{\mathrm{K}} + \mathrm{CH_3C(\overset{-}{O})CH_2COOR} \rightleftarrows \underset{\mathit{O}}{\mathrm{CH_3C(OK)CH_2COOR}} \rightleftarrows$$

$$\underset{\mathit{C}}{\mathrm{CH_3COCHKCOOR}} \rightleftarrows \mathrm{CH_3CO\overset{-}{C}HCOOR} + \overset{+}{\mathrm{K}}.$$

This conception in regard to the constitution of acetoacetic ester salts, malonic ester salts and others of this type, make clear the formation of oxygen and carbon derivatives[6] when the various salts are treated with acid chlorides, alkyl halides, benzaldehyde, etc. Oxygen salts, *O*, have long been known to react with such acid chlorides and alkyl halides; the violence and rapidity with which sodium phenyl,[1] a sodium-carbon compound, reacts with acid chlorides and alkyl halides, leaves no doubt that an acetoacetic ester salt with the constitution *C* would be very reactive. Furthermore, the writer has proved that the sodium pinaconates dissociate in ether and benzene solution as follows:

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[1] Nietzki and Schröter: Ber. d. chem. Ges., **28**, 44; **30**, 175.

[2] Ann. Chem. (Liebig), **266**, 52; **276**, 200; **277**, 59, 83, etc.

[3] J. prakt. Chem., **37**, 469; **45**, 580; **46**, 189, etc.

[4] *Vide* Claisen's discussion, Ber. d. chem. Ges., **38**, 709.

[5] Kauffmann: Ber. d. chem. Ges., **39**, 1959. Hantzsch: *Ibid.*, **39**, 1084, 3072.

[6] Nef, Michael and Claisen: *Loc. cit.*

$$\underset{1}{(C_6H_5)_2C(ONa)C(ONa)(C_6H_5)_2} \underset{K}{\rightleftarrows} \underset{2}{(C_6H_5)_2CO} + \underset{3}{(C_6H_5)_2CNa(ONa)}.$$

Reagents which will exert a *selective action* on one of the two forms of salts will aid greatly in determining if there are 2 salts in equilibrium. Benzaldehyde, carbon dioxide, etc., react readily with *3*, as they do with sodium phenyl, and *1* is transformed into *2* and *3* as fast as *3* is removed and *K* disturbed. On the other hand, acids, water, etc., react with both *1* and *3* and give a mixture of benzpinacone, about 90 per cent, benzophenone and benzhydrol. These reactions show equilibrium between the molecular forms, ions probably not coming into consideration in these reactions in benzene.

Another use of selective reagents in proving the presence of 2 tautomeric salts is the following: Phenylnitromethane and formylphenylacetic ester are tautomeric compounds, and both tautomeric forms have been isolated. If, now, the salts of these substances also exist in tautomeric forms in solution according to the following equation:

$$\overset{+}{Na} + C_6H_5\overset{-}{C}HNO_2 \rightleftarrows \underset{A}{C_6H_5CHNaNO_2} \rightleftarrows \underset{B}{C_6H_5CH : N(O)ONa} \rightleftarrows C_6H_5CH : N(O)\overset{-}{O} + \overset{+}{Na},$$

we should be able to select an acid weak enough to precipitate the more weakly acid tautomeric form, corresponding to the salt *A*, from solution, but not the stronger acid form corresponding to *B*; a strong mineral acid, however, would precipitate both tautomers. The experiments of Hantzsch and of Wislicenus amply verify this point. Carbonic acid precipitates the true phenylnitromethane[1] and parabromphenylnitromethane from solutions of their alkali salts, whereas strong acids precipitate the more strongly acid isonitro forms, nearly pure. Likewise, carbonic acid precipitates the weakly acid α-formylphenylacetic ester[2] from solutions of its salts, whereas sulphuric acid precipitates the strongly acid β-form, mixed with a small amount of the α-form. These experiments show that both tautomeric salts are present in equilibrium, with the salt of the stronger acid form, B, in excess, as we should expect.

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[1] Acree: THIS JOURNAL, **29**, 588. Ber. d. chem. Ges., **37**, 2753.

The experimental facts worked out by the writer, as well as all those of Claisen and Wislicenus, lead the writer to believe that all the syntheses analogous to the acetoacetic ester synthesis depend upon the reactions of tautomeric salts. To illustrate very briefly: It is believed that in the formation of acetoacetic ester from acetic ester and sodium ethylate the acetic ester first reacts with the sodium ethylate and forms a sodium salt of acetic ester which exists in 2 tautomeric forms. The sodium salt (2) then reacts vigorously with the acetic ester present, just as sodium phenyl or alkylmagnesium bromides do, and acetoacetic ester is formed:

$$CH_3COOC_2H_5 + NaOC_2H_5 \rightleftarrows \left\{\begin{array}{ll}(1) & CH_2 : C(ONa)OC_2H_5 \\ & \qquad \uparrow\downarrow \\ (2) & \quad CH_2NaCOOC_2H_5\end{array}\right. + C_2H_5OH;$$

$$CH_3COOC_2H_5 + NaCH_2COOC_2H_5 \rightarrow CH_3C(ONa)(OC_2H_5)CH_2COOC_2H_5 \rightarrow CH_3C(ONa) : CHCOOC_2H_5 + HOC_2H_5$$

This conception is readily applied to other similar syntheses. The reactions of

$$BrMgCH_2COOC_2H_5 \quad \text{and} \quad CH_3CH(MgBr)COOC_2H_5,^{3}$$

which probably exist in the equilibrium illustrated by the above sodium salt, bear out the above conclusions completely. This subject will be treated in great detail in a subsequent article.

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[1] Hantzsch and Schultz: Ber. d. chem. Ges., 29, 699, 2251.

[2] Wislicenus: Ann. Chem. (Liebig), 291, 147; 312, 34.

[3] Meyer and Tögel: Ann. Chem. (Liebig), 347, 55.

It is well known that when the silver salts of some amides are treated with alkyl halides at ordinary temperatures, oxygen esters are formed in large amounts, whereas the potassium salts yield, at higher temperatures, largely nitrogen esters. In some cases it has been proved that both are formed simultaneously. The copper salt of acetoacetic[1] ester, when treated with benzoyl chloride or acetyl chloride, yields a mixture of oxygen and carbon derivatives. If acetoacetic ester is heated with a mixture of silver oxide and an alkyl halide,[2] both oxygen and carbon derivatives are formed. In general, 2 different products have been found in such cases when the reaction products have been closely examined.

To account for such reactions several theories have been proposed:

I. The potassium and silver salts have different but definite structures. The potassium salt is a nitrogen compound and the silver salt is an oxygen compound (Comstock's older theory).[3]

II. When one salt yields with a certain reagent 2 products, one is formed directly and the second by rearrangement of the first (Wheeler's theory).[4] Wheeler assumed that all salts of the amides are oxygen derivatives, that these first yield O-esters which then form addition products with the alkyl halide and rearrange into N-derivatives.

III. When one salt yields with a certain reagent 2 products, one is formed by direct substitution of the metal and the other by formation of an unstable intermediate addition product (theories of Nef and of Michael).[5]

IV. The writer presents the following theory: A salt of a tautomeric compound reacts with an alkyl halide, or other reagent, and forms 2 compounds, because the tautomeric salt is really a mixture of 2 tautomeric salts in equilibrium, each of which reacts with the alkyl halide in independent side reactions. This reaction may, in certain cases, be complicated by the simultaneous rearrangement of one of the reaction products into the other or into some other product.

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[1] Nef: Ann. Chem. (Liebig), **287**, 270.

[2] Lauder: J. Chem. Soc., **77**, 738. *Vide* also Nef: Ann. Chem. (Liebig), **276**, 200.

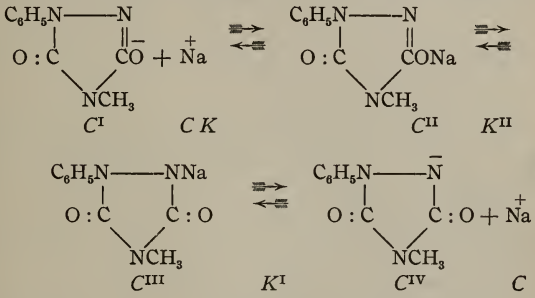
[3] Comstock and students: Ber. d. chem. Ges., **23**, 2274. THIS JOURNAL, **12**, 493; **13**, 514, 525.

[4] Wheeler and students: *Ibid.*, **21**, 187; **23**, 135; **30**, 28.

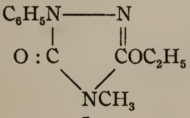
[5] Nef and Michael: *Loc. cit.*

In order to test experimentally each of the above theories the writer and his co-workers, Dr. R. F. Brunel, Mr. G. H. Shadinger and Mr. J. M. Johnson, have studied quantitatively the alkylation of some salts of tautomeric compounds, such as 1-phenyl-4-methylurazole. We have a great deal of experimental evidence supporting the view that the salts of 1-phenyl-4-methylurazole exist in solution in the following equilibrium:

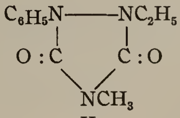
(VI.)



The values of $C, C^{I}, \ldots, K, K^{I}$, etc., vary with the salts, solvents, and the experimental conditions. When a salt of 1-phenyl-4-methylurazole is heated with ethyl iodide in water-alcohol, benzene, or ether solution, a mixture of 1-phenyl-4-methyl-3-ethoxyurazole, (I.), and 1-phenyl-4-methyl-2-ethylurazole, (II.), is formed:



I.

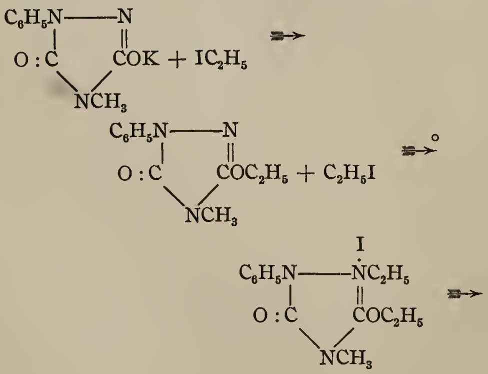


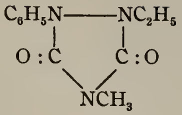
II.

(A) The ratio of these 2 products varies with the salt. The potassium salt, in 40 per cent alcoholic-water solution, gives 90 per cent N-ethyl derivative and 10 per cent O-ethyl derivative. The barium salt in the same solvent gives 93.5 per cent N-ethyl compound and 6.5 per cent O-ethyl compound. The silver salt in the same solvent gives 58.7 per cent O-ethyl derivative and 41.3 per cent N-ethyl derivative. The silver salt in ether gives 35 per cent N-ethyl compound and 65 per cent O-ethyl derivative. The measurement of these ratios at 22°, 60° and 90° shows that each ratio is nearly constant, or that the 2 side reactions have nearly the same temperature coefficient. The ratio, furthermore, does not change at different time intervals.

These facts render Comstock's older theory, I., that the silver salts are oxygen derivatives and the alkali salts nitrogen derivatives improbable. They further make it improbable that each salt is a mixture of 2 isomeric salts in a constant ratio for all the salts.

(B) Neither the O-ethyl nor the N-ethyl derivative rearranges into the other under any conditions studied. These conditions have been varied widely to include all the possible experimental conditions used in the alkylation experiments. Furthermore, since the ratio of N-ethyl and O-ethyl derivatives from a given salt does not change with time and temperature, Wheeler's theory (II.) that the O-ester is first formed directly from the salt, an oxygen compound, and then rearranges into the N-derivative, as represented by the following equations, cannot be used as a general explanation of such reactions:



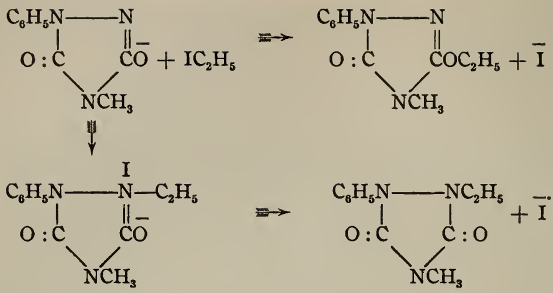


$+ C_2H_5I.$

If we represent the concentrations of urazole salt, O-ester and N-ester, by *a*, *b* and *c*, respectively, the above equation takes the form $a \xrightarrow[1]{} b \xrightarrow[2]{} c$. As will be shown in detail later, if the reactions proceed according to this equation the products *b* and *c* cannot be formed in constant ratio. The only possible way for *b* and *c* to be formed in constant ratio is: first, for reaction *2* to be instantaneous, when the value of *b* would be zero; or, second, for reaction *2* to be instantaneously reversible, when *b* and *c* would exist in constant ratio. Neither the first nor the second assumption agrees with the experimental facts. Wheeler's theory is, therefore, improbable.

The writer believes that in the case of these urazoles the O-ester and N-ester are both formed independently from the 2 salts in (VI.). In some cases, however, as Wheeler showed, this reaction is undoubtedly complicated by the simultaneous rearrangement of one product, the O-ester, into another, the N-ester, and such cases will be made subjects of investigation in this laboratory. Wheeler did not, however, prove that the rearrangement of the O-ester was rapid enough to account for all of the N-ester formed in his experiments.

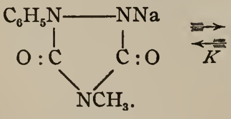
(C) The experimental evidence leads to the conclusion that only the urazole ion reacts with the ethyl iodide and that according to a reaction of the second order. According to Nef's and Michael's addition theories (III.) the salt has one structure and the O-ester and the N-ester should be formed according to the following reactions. The ethyl iodide may add to the double bond between the N and C, or add as illustrated:



This theory, however, demands that under the same conditions of solution all the different salts should give a mixture of esters in which the ratio of the O-ester to the N-ester is a constant. The metallic ion should affect the course of the reaction no more than Remsen and Reid[1] found to be the case in the hydrolysis of amides by alkalies, or than has been found in many other cases. Different salts, however, as pointed out above, give widely different ratios of O-ester to N-ester, and hence Nef's and Michael's addition theories are inadequate. Another objection which might be brought up is the constancy of the ratio of O-ester to N-ester formed over a wide range of temperature. The potassium salt gives practically the same ratio at 22°, 60° and 90°. Two such different reactions demanded by the theories of Nef and Michael might be expected to have different temperature coefficients.

(D) The writer believes that the following equations represent fairly well the reaction of such tautomeric salts with alkyl halides, the changes or manner of reaction of the ethyl iodide not being considered here. This will be taken up later in detail.

C_2



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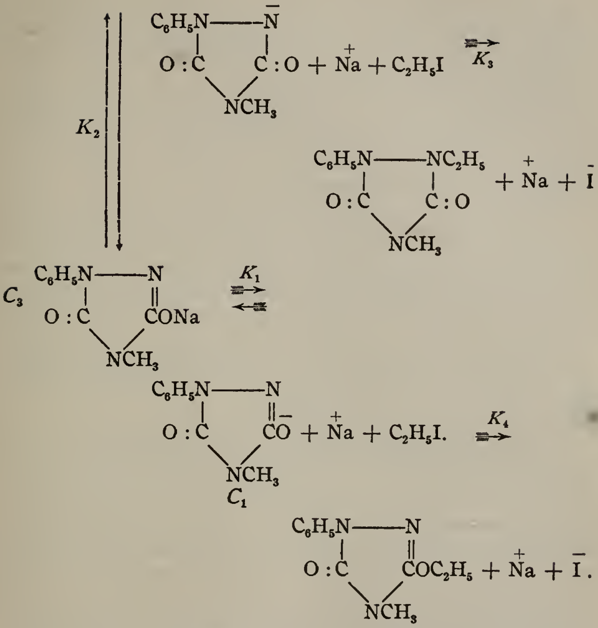
[1] This Journal, 21, 281.


K_2
K_3
C_3
K_1
K_4
C_1
C_6H_5N
$O:C$
$C:O + \overset{+}{Na} + C_2H_5I$
NCH_3
NC_2H_5
$+ \overset{+}{Na} + \overset{-}{I}$
$CONa$
$CO + \overset{+}{Na} + C_2H_5I.$
$COC_2H_5 + \overset{+}{Na} + \overset{-}{I}.$

This theory of 2 salts in equilibrium predicts that various salts will give different values for K, K_1, K_2, etc., and different ratios of O-ester to N-ester, as has been actually found by experiment. It can be shown that the ratio $C:C_1$ increases with increase in the electronegative character of the metal. In other words, a greater per cent of the silver salt is oxygen salt than is the case with the sodium salt, and this is perhaps one very important reason why a higher per cent of O-ester is obtained from the silver salt than from the sodium salt. The rate of alkylation of the various salts in equimolecular quantity is a function of their dissociation. Only the urazole ions are alkylated. The fact that different ratios of O-ester to N-ester are obtained from different salts proves that the equilibrium between the 2 tautomeric salts is an equilibrium between the molecular forms C_2 and C_3 and not between the ions C and C_1. This is exactly in accordance with the results found by Dimroth[1] in his work on ethyl 1-phenyl-5-oxy-1,2,3-triazole-4-carboxylate, who proved that the equilibrium is between the molecular enol and keto forms and not between the ions. If only the ions C and C_1 were in equilibrium we should get the same ratio of O-ester to N-ester from all the salts.

The fact that the ratio of O-ester to N-ester obtained from the potassium 1-phenyl-4-methylurazole is the same at 22°, 60° and 90° shows that the ratio of the molecular forms, K_2, does not change with the temperature. This is exactly what Dimroth found to be the case with the keto and enol forms of the ethyl 1-phenyl-5-oxy-1,2,3-triazole-4-carboxylate. The temperature coefficient of dissociation of the salts C_2 and C_3 is very small and nearly the same for all salts, as was proved by Jones and West[2] and by Noyes[3] and Coolidge.

The ratio of N-ester to O-ester, obtained from the silver salt in ether solution is 35: 65, whereas the ratio obtained in 40 per cent alcohol-water is 41 : 59. This is due either to a change in the relative reactivity of the 2 ions towards ethyl iodide or to a change in the value of K_2 with change of solvent. That the first can be great is very improbable. But that the value of K_2 can, and probably will, change with the solvent is made almost certain by the work of Dimroth,[4] who showed that the ratio of the molecular enol and keto forms of ethyl 1-phenyl-5-oxy-1,2,3-triazole-4-carboxylate is 1 : 14 in water, 1 : 150 in methyl alcohol and 1 : 300 in ethyl alcohol. The theory proposed by the writer predicts a change in ratio of the 2 salts and the esters obtained with a change in solvent, as is found to be true experimentally. Indeed, if the proper solvents and experimental conditions were chosen both forms of the salts could probably be isolated. Apparently, Hantzsch[5] made 2 isomeric salts of cyanuric acid, Titherly[6] made isomeric silver salts of benzamide and acetamide, and Wislicenus[1] apparently had isomeric copper and sodium salts of formylphenylacetic ester.

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[1] Ann. Chem. (Liebig), **335**, 1; **338**, 143.

[2] THIS JOURNAL, **34**, 357.

[3] Z. physik. Chem., **46**, 323 (1904). J. Am. Chem. Soc., **26**, 134 (1904).

[4] *Loc. cit.*

[5] Ber. d. chem. Ges., **35**, 2717 (1902).

[6] J. Chem. Soc., **79**, 409 (1901).

The theory proposed predicts that, as Remsen and Hillyer[2] and Lengfeld[3] found, different alkyl halides will have different reaction coëfficients, K_3 and K_4, and that the ratio of O-ester to N-ester obtained from a given salt may vary with different alkyl halides. This has been found true experimentally; whereas 0.3 N solution of potassium salt in 40 per cent alcohol-water containing equimolecular quantity of ethyl iodide reacted at 60° in 1 hour to the extent of 30.35 per cent, and 90 per cent of the reaction product was N-ester, the potassium salt and ethyl bromide, under exactly the same conditions, reacted to the extent of 22.5 per cent and 87.7 per cent of the reaction product was N-ester.

JOHNS HOPKINS UNIVERSITY,
June, 1906.

Contribution from the Texas Experiment Station.

A SIMPLE FAT EXTRACTION APPARATUS.[4]

BY G. S. FRAPS.

This is a mercury sealed apparatus, simple in construction, cheap and easy to operate. Several pieces of this apparatus have been in use in the Texas Experiment Station since the fall of 1905 and have given satisfactory results.

The apparatus is represented in the accompanying drawings. Fig. I. shows the apparatus set up ready for use. Fig. II. is the vessel used for extraction. It is fitted with a fat extraction cartridge. Fig. III. represents a flask which is similar to Knorr's flask. Fig. IV. is a condenser. The water enters A and leaves at B. The cork C should have openings made in it, otherwise the mercury may be thrown out of the flask when the extraction is begun. Fig. V. is a straight glass jacket, 1 inch in outside diameter. The two prongs at the lower end of the tube serve to hold the flask for the fat by means of rubber bands, if desired. We never employ them.

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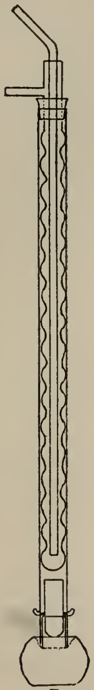
[1] Ann. Chem. (Liebig), **291**, 147.

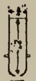
[2] THIS JOURNAL, **8**, 251.

[3] *Ibid.*, **11**, 40.

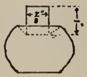
[4] The apparatus has some points of resemblance to Knorr's, described in Wiley's "Principles and Practice of Agricultural Analysis," 1 Ed., Vol. III., pp. 44-47, but is much simpler, is only one-third as costly and any part may be replaced at slight expense.



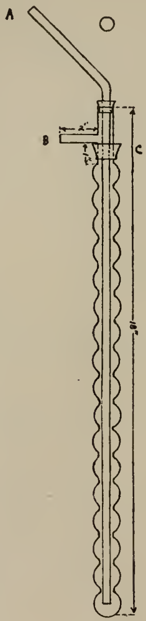
I



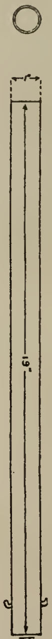
II



III



IV



V

In using the apparatus the substance is placed in the tube and dried. It is then fitted in the neck of the flask, Fig. III, and the apparatus set up as shown in Fig. I. The depression in the flask is filled with mercury. The amount of ether required depends upon the atmospheric temperature. In cool weather a small quantity suffices for the extraction. The relative dimensions of the several pieces are shown in the drawings. They can, of course, be modified very easily if desired. A siphon arrangement can be used in place of the capsule, Fig. II.; in such case the jacket, Fig. V., must be made a little longer.

Contributions from the Chemical Laboratory of Harvard College.

ON THE CONSTITUTION OF THE α- AND β-ADDITION COMPOUNDS OF ALCOHOLS AND TETRABROMORTHOBENZOQUINONE.[1]

By C. Loring Jackson and R. D. MacLaurin.

In 1904 Horace C. Porter and one of us[2] described 2 series of addition compounds formed by the union of tetrabromorthobenzoquinone with alcohols, the general formula for each of which was $(C_6Br_4O_2)_2.ROH$. The first (α) series was formed by the direct action of the alcohols on the quinone in the cold. Its members were characterized by crystallizing in needles, which turned red on melting from the formation of hexabromorthoquinopyrocatechin ether, $C_6Br_4O_2.C_6Br_2O_2$, and by conversion into the corresponding member of the β-series by boiling with a dilute solution of sodic hydrate, or, less conveniently, by the regulated action of acetic anhydride. We have found that the same change is brought about with the methyl compound by warming it with a mixture of benzene, hydroxylamine hydrochloride and sodic carbonate, and this seems to be an even better method of making this β-compound than that with sodic hydrate. The members of the β-series are characterized by crystallizing in rhombic plates, which melt to a colorless liquid, and by an unusual stability.

In the first paper[3] on this subject, reasons were given for reducing the possible structural formulas for the α-alcohol compounds to two:

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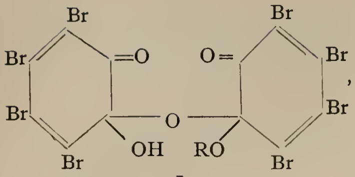
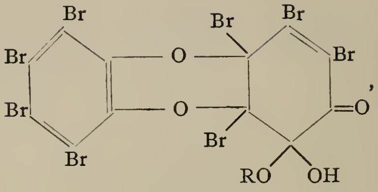
[1] The work described in this paper formed part of a thesis presented to the Faculty of Arts and Sciences of Harvard University for the degree of Doctor of Philosophy by Robert D. MacLaurin.

[2] This Journal, 31, 89 (1904).

[3] *Ibid.*, 31, 92 (1904).



I.



II.

which will be briefly recapitulated here. The 2 benzene rings cannot be united by the carbon atoms either of the rings themselves or of the added substance, as the compounds thus formed would be too stable to drop by mere heat into the hexabromorthoquinopyrocatechin ether, $C_6Br_4O_2.C_6Br_2O_2$; they must therefore be united by the oxygen either directly, as in the above formulas, or with the added substance taking part in the union; this latter method of union must be rejected, because there is a water compound resembling the alcohol compounds most closely, and, if the union is effected through the quinone oxygen and the carbon of the alcohol, this water compound must have an entirely different structure from the alcohol bodies. If, on the other hand, all these substances have the same structure, which can hardly be doubted, and the added body takes part in the union, it must take place through chains of oxygen atoms, giving a structure much less stable than that of the α-compounds. The rejection of the second supposition—that the carbon of the alcohol takes part in the union—is supported by the observation that the benzyl alcohol compound gave no benzoic acid when decomposed with hydrobromic acid, whereas this product must have been formed with such an arrangement of the molecule.

Neither in the paper by Porter (just cited) nor in that of Carlton,[1] nor of Russe,[2] was any convincing argument given for deciding whether Formula I. or II. was the correct one. Such an argument we have found in the conversion of an α- into a β-compound by the regulated action of acetic anhydride, but before giving it we must discuss a change in Formula II., rendered necessary by our study of the action of sodic hydrate, in aqueous solution, on hexachlororthoquinopyrocatechin ether, which yielded hexachlordihydroxypyrocatechin ether and sodic chloranilate by the following reactions:

$$2C_6Cl_4O_2.C_6Cl_2O_2 + 6NaOH =$$

$$2C_6Cl_4O_2H_2 + 2C_6Cl_2O_2Na_2O_2 + 2NaOH =$$

$$C_6Cl_4O_2.C_6Cl_2O_2H_2 + 2NaCl + 2H_2O + 2C_6Cl_2O_2Na_2O_2.$$

That tetrachlorpyrocatechin is converted into hexachlordihydroxypyrocatechin ether by the action of a warm solution of sodic hydrate was proved by a special experiment.

That the sodium salt formed in this reaction is derived from chloranilic acid, and not from an isomeric dioxyortho- or paraquinone, was proved by a careful comparison of it[3] with chloranilic acid made from chloranil. This comparison may be divided into 3 parts:

1. The determination of the water of crystallization in the 2 acids and several of their salts with the following results:

$$C_6Cl_2(OH)_2O_2.2H_2O; \quad C_6Cl_2(OK)_2O_2.H_2O.$$

(The potassium salt from orthoquinone also crystallized with $2H_2O$.)

$$C_6Cl_2(ONa)_2O_2.3H_2O.$$

(Valeur[4] found that sodic chloranilate crystallizes at 35° with $4H_2O$, at ordinary temperatures with $3H_2O$. Six of our determinations gave percentages for $3H_2O$, one gave an amount not far from $4H_2O$.)

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[1] This Journal, **34**, 422 (1905).

[2] *Ibid.*, **35**, 154 (1906).

[3] For much of this comparative work the material was derived from tetrachlororthoquinone and methyl alcohol, instead of from the hexachlor ether.

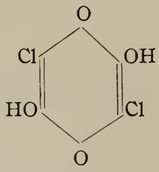
[4] Ann. Chim. Phys., [7], **29**, 507.

$$C_6Cl_2O_2BaO_2.3H_2O.$$

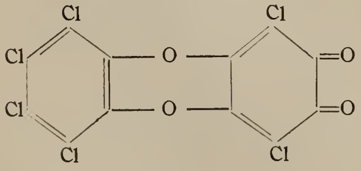
In every case the salt of the acid from the orthoquinone was identical in appearance with that from chloranil.

2. The behavior of the ammonium salts of the 2 acids was studied with a number of reagents. In each case the color of the precipitates was the same and, as many of these colors are very striking, this is a strong proof of their identity.

3. The silver salt of the acid from the orthoquinone was converted into the dimethyl ether by treatment with methyl iodide. This melted at 141°–142°, the melting point given by Kehrmann[1] for the 3,6-dichlor-2,5-dimethoxyquinone prepared from chloranilic acid. These comparisons leave no doubt that the second product of the action of sodic hydrate on hexachlororthoquinopyrocatechin ether is the sodium salt of chloranilic acid. Chloranilic acid has the constitution[2]



and it follows from this that the formula of the hexachlor ether must be symmetrical (III., not IV.).



III.

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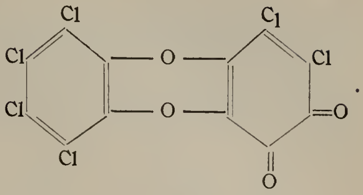
[1] J. prakt. Chem. [2], **40**, 370.

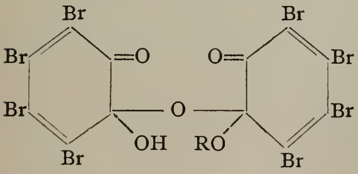
[2] Hantzsch: Ber. d. chem. Ges., **20**, 1303 (1887). Hantzsch and Schniter: *Ibid.*, **20**, 2280.



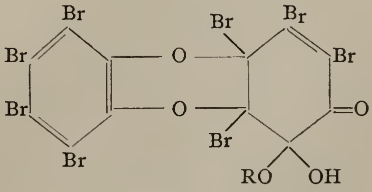
IV.

The hexabrom ether resembles the hexachlor so strongly in every respect that it must have a similar symmetrical structure, and this inference was confirmed by treating it with a warm solution of sodic hydrate, when sodic bromanilate was formed. This was identified by its properties and an analysis of the free acid, as more work did not seem worth while after the thorough identification of the chloranilic acid given above.

We now return to Formulas I. and II. for the alcohol addition compounds of the α-series.



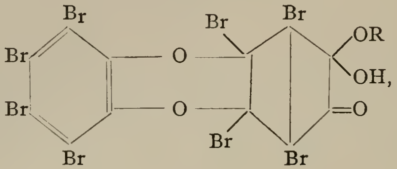
I.



II.

Formula II. owes its justification only to the fact that these α-bodies, when heated, pass easily into the hexabrom ether, $C_6Br_4O_2.C_6Br_2O_2$, but if this ether has the symmetrical structure

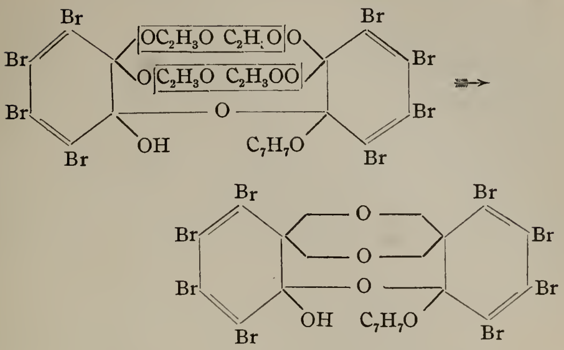
III., a substance constituted as in II. could pass into it only by the most improbable transformations, so that this formula must be rejected. If we try to save the principle embodied in II. by converting it into a symmetrical formula, we encounter difficulties in the arrangement of the bonds, as the only possible form, V.,



V.

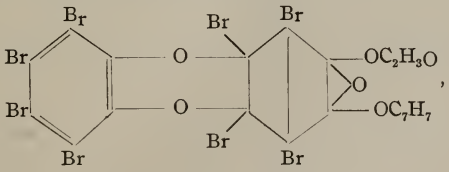
does not conform to Kekulé's theory of the benzene ring. But in spite of this it is not impossible, especially when the occurrence of para chains among the terpenes is remembered. On the other hand, a configuration such as this para bond, which does not come under the prevailing theory, or, in other words, which is not in harmony with most of the observed facts of the science, is certainly a strong, although not conclusive argument against the adoption of such a formula.

The proof that Formula V. is not correct rests on the formation of the β-benzyl compound, by the regulated action of acetic anhydride on the α-body, which can be explained with Formula I., but is impossible with V. With Formula I. this action can take place by the addition of 2 molecules of acetic anhydride to the 2 quinone oxygen atoms, and the subsequent removal of them as shown below. Such an addition of acetic anhydride, followed by its removal without any change in the conditions, may be brought about by the natural tendency to form such a very stable product as the β-compound, or, if it is less soluble than the intermediate acetacetal, there would be nothing strange in its formation:



VI. β.

The formula (VI.) for the β-compounds, to which this course of reasoning leads, is certainly a strange one, but we have not succeeded in finding any other which will represent the formation of the free (not acet) β-compound by this reagent, and the other reactions for the formation of the β-compounds also lead naturally to this same formula. On the other hand, we cannot explain the conversion of the α- into the β-compound by acetic anhydride, if Formula V. is adopted. The formation of an acet compound does not offer any difficulty,



VII.

but actually the product is the hydroxy, not the acet compound, and the acet body, if formed at first, could not be converted into the hydroxy compound by the action of cold water, or methyl alcohol, or benzene (the only agents used with it in this case), since this acet body[1] has been made by the action of boiling acetic anhydride on the β-compound, and proved to be stable even with sodic hydrate.

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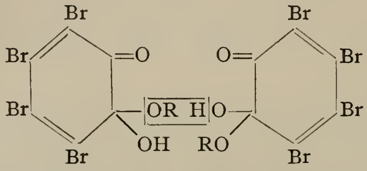
[1] Jackson and Carlton: This Journal, 34, 440 (1905).

The proof of the accuracy of Formula I., given in the preceding paragraph, is supported by the 2 following arguments, which, by themselves, are almost sufficient to establish the constitution of these bodies.

The formation of the α-compound by the action of the alcohol on the quinone in the cold can be explained according to Formula I., as follows: The quinone is first converted into a hemiacetal, and then 2 molecules of this split out a molecule of the alcohol, thus:



These reactions suppose an addition of the alcohol followed by a removal of it without any change in the conditions, as in the case just discussed, but, if the α-body is much less soluble than the hypothetical hemiacetal, there is nothing strange in this supposition. On the other hand, the formation of a substance having Formula V. is inexplicable. Why should the presence of an alcohol, whether it form a hemiacetal or not, cause the opening of a double bond and the addition of $C_6Br_4O_2$ to the benzene ring? The formation of such a compound shows, it is true, a certain analogy to the formation of quinhydrones, but this rather tells against this formula than its favor, as all quinhydrones known are strongly colored (the octobromorthoquinhydrone being black[1]), so that the white or yellowish-white α-bodies can hardly be related to them.

The β-compounds melt without decomposition and show a very slight tendency to give up bromine with reagents. For instance, the β-methyl compound showed no sign of decomposition after being boiled with an alcoholic solution of sodic ethylate for an hour, whereas tetrabromorthoquinone was attacked at once. This striking stability is explained by Formula VI. derived from I., but not by any expression we have been able to derive from Formula V., as it does not seem possible that 2 atoms of bromine[1] could be held firmly, when exposed to the loosening action of oxygen attached to the same carbon and of acetal groups in the para position, especially when the similar atoms of bromine in the α-body (V.) are easily removed by the action of heat. It is true that the quino and hemiacetal groups of the α-body (V.) have been converted into hemiacetal and acetal groups in the β-, but, although this would diminish their loosening effect on the bromine, it is not possible that it would entirely destroy it, and even fix these atoms of bromine more firmly than in the tetrabromorthoquinone.

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[1] Jackson and Russe : This Journal, **35**, 176 (1906).

The one reaction of these substances, which is explained better by V. than by I., is the conversion of the α-compound into hexabromorthoquinopyrocatechin ether by heat. If I. is the true formula, the molecule must split into 2 molecules of tetrabromorthoquinone and 1 of the alcohol, which then, by the loss of 2 atoms of bromine and the alcohol, give the hexabrom ether. That tetrabromorthoquinone is converted by heat into the hexabrom ether, $C_6Br_4O_2.C_6Br_2O_2$, has been determined by a special experiment,[2] which we have verified more recently. The ether obtained in this case is less pure than that from the action of heat on an α-compound, but this is undoubtedly explained by the effect of the alcohol in the latter case, which would promote the formation of the ether by converting part of the tetrabromorthoquinone into tetrabrompyrocatechin.

For greater clearness we add a brief recapitulation of our reasons for rejecting Formula V., thus proving that Formulas I. and VI. are those of the α- and β-compounds. (1) The regulated action of acetic anhydride converts the α-benzyl compound into the free (not acet) β-compound. Formula V. could give only the acet β-compound under these conditions. (2) Formula V. is not in harmony with Kekulé's theory of the benzene ring. (3) The formation of a substance with Formula V. from an alcohol and tetrabromorthoquinone is inexplicable. (4) The β-compound derived from Formula V. must be an unstable substance. As a matter of fact, the β-compounds are remarkably stable. According to Formulas I. and VI. the names of the methyl compounds would be, for the α-body octobromorthoquino-1-methoxy-1′-hydroxy-1-monoxide; for the β-compound, octobromorthoquino-1-methoxy-1′-hydroxy-1,2,2-trioxide.

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[1] The hydroxyl compound corresponding to Formula VII. shows the position of these 2 atoms of bromine.

[2] Jackson and Porter: THIS JOURNAL, 31, 118 (1904).

Since the symmetrical structure of the hexabromorthoquinopyrocatechin ether has been established, it follows that Shaffer's[1] addition compound,

$$C_6Br_4O_2.C_6Br_2O_2.(CH_3OH)_2,$$

and the heptabromhemiether of Russe,[2]

$$C_6Br_4OHO.C_6Br_3O_2,$$

must also have a symmetrical structure.

Some preliminary experiments are also described in the body of the paper, which have given promising results.

EXPERIMENTAL.

Action of Sodic Hydrate on Hexachlororthoquinopyrocatechin Ether.

If a 10 per cent solution of sodic hydrate was added to the hexachlororthoquinopyrocatechin ether, $C_6Cl_4O_2.C_6Cl_2O_2$, in quantity, there was formed almost immediately a deposit of purplish-black, short, stout needles, which seemed to be an addition compound of the ether and sodic hydrate, as dilute sulphuric acid regenerated the ether and an analysis of the crystals, with no other purification than washing with water, gave 3.98 per cent of sodium, which is not very far from 4.98, the amount of sodium in $C_{12}Cl_6O_2.NaOH$. If, on the other hand, the sodic hydrate was added gradually, a different result was obtained. For this purpose 2 grams of hexachlororthoquinopyrocatechin ether, $C_6Cl_4O_2.C_6Cl_2O_2$, were warmed with 50 cc. of water in an evaporating dish on the steam-bath and single drops of a 10 per cent solution of sodic hydrate added at frequent intervals. A reaction began after the addition of a few drops and was brought to an end by continuing the heating and addition of sodic hydrate for an hour. The total quantity of sodic hydrate used, however, did not exceed 30 drops. The products of the reaction were hexachlordihydroxypyrocatechin ether, identified by its brown color, melting point of 290°, and conversion by nitric acid into the red orthoquino ether, $C_6Cl_4O_2.C_6Cl_2O_2$, and sodic chloranilate, recognized by its color, crystalline form, and the following analysis of the salt purified by 2 recrystallizations from water.

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[1] THIS JOURNAL, **34**, 460 (1905).

[2] *Ibid.*, **35**, 156 (1906).

0.3456 gram of the air-dried salt lost, at 110°, 0.0614 gram H_2O and gave 0.1597 gram of Na_2SO_4.

	Calculated for $C_6Cl_2(ONa)_2O_2.3H_2O$.	Found.
H_2O	17.59	17.76

	Calculated for $C_6Cl_2(ONa)_2O_2$.	Found.
Na	18.19	18.20

In the reaction described above the hexachlordihydroxypyrocatechin ether must have been formed from the tetrachlorpyrocatechin resulting with the sodic chloranilate from the decomposition of the orthoquino ether. It seemed important, therefore, to determine whether tetrachlorpyrocatechin underwent such a reaction in presence of sodic hydrate. Accordingly, 1 gram of tetrachlorpyrocatechin was warmed on the steam-bath with dilute sodic hydrate, and in the course of a few minutes chocolate-brown needles appeared, which showed the melting point, 290°, of the hexachlordihydroxy ether and were converted by nitric acid, quantitatively, into the orthoquino ether. There can be no doubt, therefore, that they were this substance.

As one of the most important arguments in regard to the constitution of our orthoquinone derivatives is based on this formation of chloranilic acid, we give the proof that our product was this substance and not an isomeric dihydroxyquinone. It was first encountered as one of the products of the action of methyl alcohol on tetrachlororthoquinone, and in the beginning we hoped it might be a dihydroxyorthoquinone, which must be the immediate product of the reaction either with methyl alcohol or sodic hydrate. To establish its identity we analyzed the acid and a number of its salts, and for the sake of absolute certainty, made parallel analyses of the corresponding compounds derived from chloranil in the usual way.

Chloranilic acid from chloranil and the substance from tetrachlororthoquinone and methyl alcohol, or the red ether and sodic hydrate, crystallized from water in reddish brown, hexagonal plates, which sublimed in open tubes without melting, and with water gave the characteristic purple solution. They were dried on filter paper for analysis. In these analyses the substance from orthoquinone will be called *a*, that from chloranil *b*.

I. 0.2350 gram substance *a*, when heated to 110°, lost 0.0343 gram H_2O.

II. 0.3580 gram substance *a* lost 0.0512 gram H_2O.

III. 0.4226 gram substance *b* lost 0.0593 gram H_2O.

IV. 0.3027 gram substance *b* lost 0.0426 gram H_2O.

	Calculated for $C_6Cl_2(OH)_2O_2.2H_2O$.	Found.			
		I.	II.	III.	IV.
		a.		*b*.	
H_2O	14.69	14.60	14.30	14.04	14.07

In experiment II. it was found that 13.91 per cent of the water went off by drying in the air. Both substances sublimed without melting in open tubes and gave the characteristic purple solution with water.

The dark, purplish-red needles of the potassium salt, after crystallization from water, were dried *in vacuo*.

I. 0.1342 gram substance *a*, when heated to 110°, lost 0.0085 gram H_2O.

II. 0.1994 gram substance *a* lost 0.0118 gram H_2O.

III. 0.3582 gram substance *b* lost 0.0215 gram H_2O.

IV. 0.2456 gram substance *b* lost 0.0143 gram H_2O.

V. 0.1023 gram substance *a* gave 0.0976 gram AgCl.

	Calculated for $C_6Cl_2(OK)_2O_2.H_2O$.	Found.				
		I.	II.	III.	IV.	V.
		a.		*b*.		*a*.
H_2O	5.94	6.33	5.92	5.95	5.82	. .
Cl	23.43	. .	. .	. .	. .	23.59

I. 0.1876 gram substance *a*, dried at 110°, gave 0.1143 gram K_2SO_4.

II. 0.3369 gram substance *b* gave 0.2046 gram K_2SO_4.

	Calculated for $C_6Cl_2(OK)_2O_2$.	Found.	
		I.	II.
		a.	*b*.
K	27.44	27.35	27.27

The salt from tetrachlororthoquinone was also observed with 2 molecules of water.

I. 0.3027 gram salt *a*, dried *in vacuo*, when heated to 110°, lost 0.0335 gram H_2O.

II. 0.2096 gram salt *a* lost 0.0225 gram H_2O.

III. 0.2304 gram salt *a*, dried *in vacuo*, gave 0.1267 gram K_2SO_4.

IV. 0.2278 gram salt *a* gave 0.2070 gram AgCl.

	Calculated for $C_6Cl_2(OK)_2O_2.2H_2O$.	Found.			
		I.	II.	III.	IV.
		a.			
H_2O	11.20	11.06	10.73	.	. .
K	24.34	. .	. .	24.64	. .
Cl	22.12	. .	. .	. .	22.47

0.1871 gram salt *a*, dried at 110°, gave 0.1132 gram K_2SO_4.

	Calculated for $C_6Cl_2(OK)_2O_2$.	Found.
		a.
K	27.44	27.17

Probably the potassium salt from chloranil could also have been obtained with 2 molecules of water, but we did not think it worth while to search for this combination.

The dark red needles of the sodium salt were dried in the air for analysis:

I. 0.4432 gram salt *a*, dried at 110°, lost 0.0789 gram H_2O.
II. 0.3472 gram salt *a* lost 0.0631 gram H_2O.
III. 0.2555 gram salt *a* lost 0.0470 gram H_2O.
IV. 0.2509 gram salt *a* lost 0.0541 gram H_2O.
V. 0.2409 gram salt *b* lost 0.0419 gram H_2O.
VI. 0.2801 gram salt *b* lost 0.0503 gram H_2O.

	Calculated for $C_6Cl_2(ONa)_2O_2.3H_2O$.	Found.					
		I.	II.	III.	IV.	V.	VI.
		a.				*b*.	
H_2O	17.59	17.80	18.18	18.39	21.57	17.39	17.95

Valeur[1] obtained the sodic chloranilate at ordinary temperatures with $3H_2O$, at 35° with $4H_2O$. Our 6 determinations, all but IV., agree with the salt with $3H_2O$. IV. approaches the percentage required by $4H_2O$, which is 22.15.

I. 0.3643 gram salt *a*, dried at 110, gave 0.2047 gram Na_2SO_4.
II. 0.2298 gram salt *b* gave 0.1283 gram Na_2SO_4.

	Calculated for $C_6Cl_2(ONa)_2O_2$.	Found.	
		I. *a.*	II. *b.*
Na	18.19	18.20	18.09

The fawn-colored barium salt, purified by washing with hot distilled water, was dried in the air for analysis:

I. 0.2395 gram salt *a*, air-dried, lost at 110°, 0.0329 gram H_2O.
II. 0.2404 gram salt *a* lost 0.0339 gram H_2O.
III. 0.2859 gram salt *b* lost 0.0376 gram H_2O.
IV. 0.3694 gram salt *b* lost 0.0497 gram H_2O.

	Calculated for $C_6Cl_2O_2BaO_2.3H_2O$.	Found.			
		I.	II.	III.	IV.
		a.		*b.*	
H_2O	13.58	13.74	14.10	13.15	13.46

I. 0.2066 gram salt *a*, dried at 110°, gave 0.1395 gram $BaSO_4$.
II. 0.2483 gram salt *b* gave 0.1679 gram $BaSO_4$.

	Calculated for $C_6Cl_2O_2BaO_2$.	Found.	
		I. *a.*	II. *b.*
Ba	39.82	39.69	39.76

The behavior of dilute ammoniacal solutions of the 2 substances with various reagents was found to be identical, giving the following striking reactions with salts of the metals named:

Barium, Strontium, brown precipitate.
Magnesium, brown needles with tapering ends.
Zinc, pinkish white.
Cadmium, yellowish brown.
Cobalt, groups of pale purple needles.
Nickel, grass-green precipitate.
Lead, fawn color.
Copper, bluish green.

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[1] Ann. Chim. Phys., [7], **29**, 507.

Bismuth, dark blue.
Silver, dark brown, fern-shaped crystals.

Finally, the substance from tetrachlororthoquinone was converted into its dimethyl ether by adding argentic nitrate to a dilute ammoniacal solution of it and heating the dry, brown silver salt to 100° with the calculated quantity of methyl iodide, in a sealed tube, for 2 hours. The product, after crystallization from hot benzene, melted at 141°–142°, the melting point of the 3,6-dichlor-2,5-dimethoxyparaquinone, according to Kehrmann.[1] There can be no doubt, therefore, that the substance obtained from haxachlororthoquinopyrocatechin ether and sodic hydrate, or from tetrachlororthoquinone by the action of methyl alcohol is chloranilic acid, which must have been formed from the dihydroxyorthoquinone—the first product of the reaction—by the familiar shifting from an oxyorthoquinone to a derivative of the para series.

Formation of Bromanilic Acid from Hexabromorthoquinopyrocatechin Ether.

Two grams of the hexabromorthoquinopyrocatechin ether were allowed to stand with a dilute solution of sodic hydrate over night, when long, purplish red needles were deposited. These were acidified with dilute sulphuric acid, recrystallized from water twice and dried for analysis:

0.1823 gram substance gave 0.2302 gram AgBr.

	Calculated for $C_6Br_2(OH)_2O_2$.	Found.
Br	53.69	53.73

The substance was recognized as bromanilic acid by its color and crystalline form, the purple solution which it formed with water, and the nearly black prisms of the sodium salt.

Action of Heat on Tetrabromorthoquinone.

Porter[2] found that when tetrabromorthoquinone was heated bromine was given off and hexabromorthoquinopyrocatechin ether formed, but the ether made in this way contained a white impurity, which was not further studied. We have repeated this experiment and obtained the ether, and have also tried the action of heat on tetrachlororthoquinone, which gives the hexachlor ether even more easily.

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[1] J. prakt. Chem., [2], 40, 370.

[2] THIS JOURNAL, 31, 118 (1904).

Behavior of the β-Addition Compound, Octobromorthoquino-1-methoxy-1′-hydroxy-1-2,2-trioxide with Sodic Ethylate.

When the β-compound, $(C_6Br_4O_2)_2.CH_3OH$, was heated with a strong alcoholic solution of sodic ethylate, during the first hour there was no visible action, but after the mixture had been heated 10 hours, dark-colored products were formed and tests obtained for bromide and pyrocatechin. The β-compound is, therefore, much less easily affected by sodic hydrate than tetrabrompyrocatechin, which reacts with it at once, somewhat even in the cold, very readily when heated.

The β-addition compound, $(C_6Br_4O_2)_2.CH_3OH$, when heated with amyl alcohol and metallic sodium, seemed to be completely decomposed in about 10 minutes. Tests were obtained for bromide and pyrocatechin.

Action of Hydroxylamine on the α-Addition Compound, Octobromorthoquino-1-methoxy-1′-hydroxy-1-monoxide.

One gram of the addition compound was dissolved in benzene and mixed with the hydrochloride of hydroxylamine and sodic carbonate. Upon warming the mixture on the steam-bath, glistening white leaflets began to separate almost immediately, which were filtered out and washed with water, when they were found to melt at 259°–260°. One crystallization from a mixture of equal parts of benzene and chloroform raised the melting point to 261°–262°, when the substance was dried and analyzed:

0.2398 gram substance gave 0.4094 gram AgBr.

	Calculated for $(C_6Br_4O_2)_2.CH_3OH$.	Found.
Br	72.73	72.64

As the substance crystallizes in white rhombic plates and melts at 261°–262° to a colorless liquid, there can be no doubt that it is the β-methyl alcohol compound. This seems to be a remarkably good way of making this substance, as the yield is quantitative and the product essentially pure.

The following experiments were tried in the hope of getting new data for the determination of the constitution of the α-bodies. In no case did they go beyond the preliminary stage, and it must be understood, therefore, that all the results are subject to revision.

Action of Acetic Anhydride on the α-Methyl Compound, $(C_6Br_4O_2)_2.CH_3OH$.—Two grams of the α-methyl compound were shaken with 15–20 cc. of acetic anhydride for 15 minutes and then allowed to stand at ordinary temperatures for several hours, when it was found that the solid had turned yellow. This product was filtered out, washed with ligroin and recrystallized 4 times from a mixture of equal parts of benzene and ligroin, when it showed the constant melting point 225°.

0.1941 gram substance gave 0.3321 gram AgBr.

	Calculated for $(C_6Br_4O_2)_2.CH_3OH$.	Found.
Br	72.73	72.81

If this is not a mixture of the α- and β-isomers but a definite compound, it is the first representative of a new—γ—class of bodies, as it melts at 225°, whereas the α-body melts at 178°–182°, the β-compound at 261°. That the substance is not such a mixture is indicated by the following observations: Its yellow color, its constant melting point, the formation of a brownish-red substance on melting instead of the bright red given by the α-compounds, the fact that it crystallizes in needles from ligroin, and in clustered plates from benzene and ligroin, whereas the plates of the β-compound do not occur in clusters, and its greater solubility in organic solvents.

Properties.—It crystallizes in clusters of yellow plates, which turn brownish-red and melt at 225°. It is easily soluble in ethyl or methyl alcohol, ether, acetone, ethyl acetate, benzene, or toluene; slightly soluble in ligroin. Strong sulphuric acid has no effect on it in the cold and only a slight one when hot. Neither strong nitric acid nor strong hydrochloric acid acts on it. Sodic hydrate dissolves it and the solution gives a white precipitate with dilute sulphuric acid. Ammonic hydrate turns it white and dissolves it slightly.

A white product, melting with reddening at 218°, was also formed in the reaction described above, but we can say nothing about its composition.

By the action of warm acetic anhydride a white product, melting at 138°–140°, and by longer action one melting and reddening at 195°, and, finally, hexabromorthoquinopyrocatechin ether were formed.

The object of this work was to isolate some of the intermediate products formed in the conversion of the α- into the β-compound. While the substance analyzed does not seem to be one of these, it is possible that some of the others may be the compounds sought; the examination of them will, therefore, be continued in this laboratory.

Action of Acetic Anhydride on the α-Water Compound, $(C_6Br_4O_2)_2.H_2O$.—This work was taken up in order to prepare and analyze the β-water body, which Porter[1] thought he had made, but, as no analysis was attempted, its nature was inferred from its properties, especially the facts that it crystallized in rhombic plates and melted at 221°–222° without visible decomposition. Our first experiments were tried with small quantities of acetic anhydride and sodic acetate, according to the directions of Porter, but as they gave principally the ether, $C_6Br_4O_2.C_6Br_2O_2$, we modified the conditions as follows: Two grams of the α-water compound were treated with enough acetic anhydride for complete solution, dried sodic acetate was then added and the mixture warmed on the steam-bath for 15–20 minutes, when only a small amount of the red ether was formed; 800 cc. of water were now added and the pale purple solution heated on the steam-bath until a white precipitate was thrown down, which was filtered off and recrystallized from a mixture of methyl alcohol and benzene, until it showed the constant melting point 240°, when it was dried for analysis:

I. 0.1807 gram substance gave 0.3234 gram AgBr.

II. 0.1711 gram substance gave 0.3096 gram AgBr.

III. 0.1899 gram substance gave 0.1284 gram CO_2 and 0.0424 gram H_2O.

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[1] THIS JOURNAL, 31, 110 (1904).

	Calculated for		Found.		
	$C_{12}Br_8O_3$.	$C_{12}Br_8O_4$.	I.	II.	III.
Br	76.92	75.48	76.15	77.03	. .
C	17.31	16.98	. .	. .	18.45
H	. .	. .	. .	. .	2.48

From the analyses alone the preference must be given to the formula $C_{12}Br_8O_3$, but we are inclined to think that its real formula is $C_{12}Br_8O_4$, because we cannot see how a substance containing O_3 could be formed from the *α*-compound, whereas the second formula would be the natural result of the complete application of the reaction by which *β*-compounds are formed from *α*-bodies. This point can be settled only by more analytical work.

Our substance is probably different from that obtained by Porter, as it melts at 240° instead of 221°–222°. It may well be that Porter's substance was the *β*-water compound, of which this is the anhydride. We hope that this interesting substance will be submitted to a thorough study in this laboratory in the near future.

Properties.—It crystallizes in white, polygonal plates, which melt at 240° without change of color. It is soluble in benzene; slightly soluble in acetone, ethyl acetate or toluene; essentially insoluble in alcohol or ligroin. The best solvent for it is a mixture of benzene and methyl alcohol. Cold, strong sulphuric acid has no effect on it, but when hot a faint reddish-brown solution is obtained. Strong nitric acid, strong hydrochloric acid, or sodic hydrate has no effect on it, hot or cold. Acetic anhydride has no further action on this substance, which is in accord with the formula $C_{12}Br_8O_4$.

Oxidizing agents, as a rule, have but little action on the *β*-compounds,[1] and in confirmation of this fact we found the methyl compound entirely unaltered by bromine and water. Hot, fuming nitric acid, on the other hand, acts upon it, giving, under carefully regulated conditions, a yellow oil and oxalic acid. In the cold, substances melting at 275°–280°, 230°, 100°–102° and oxalic acid were obtained. When the corresponding *β*-chlor compound, $(C_6Cl_4O_2)_2.CH_3OH$, was treated with fuming nitric acid it behaved in a similar way, giving a yellow oil and oxalic acid. The yields of all these bodies were so exceedingly small that the investigation of them will be very laborious.

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[1] This Journal, 34, 441 (1905).

Phenylhydrazine acted on the α-methyl body,

$$(C_6Br_4O_2)_2.CH_3OH,$$

even when gently warmed in alcoholic solution with it. In different experiments 2 products were obtained, one melting at 155°–156°, the other constant at 200°. Analyses of this latter product gave Br 36.20; N 15.49, 15.48; C 31.68; H 6.98; but we are unable to derive any formula from these percentages, as the number of atoms of carbon is only little more than twice the number of atoms of nitrogen. The substance, apparently, gives up phenylhydrazine easily to alkalies or acids.

Phenylhydrazine acts readily with the β-methyl compound, $(C_6Br_4O_2)_2.CH_3OH$, even when diluted with alcohol, which is strange in view of the marked stability of this compound toward other reagents, especially aniline. In the preliminary experiments 3 different products were obtained, one melting at 225° and giving Br 5.05; N 17.1 per cent; another melting at 162° and giving a test for halogen; and a third (made by the action of undiluted phenylhydrazine), which was free from halogen. Pyridine also acts on this β-compound, giving a brown product.

CAMBRIDGE, MASS.,
October 8, 1906.

NOTE.

Dry Method for the Generation of Oxygen from Sodium Peroxide.

The action of water on fused sodium peroxide is one of the most convenient and elegant methods for the preparation of oxygen for laboratory or lecture purposes. The liberation of the gas is so lively, however, that a specially constructed generator is usually required to enable one to control the evolution of it. To prepare a small quantity, the most efficient method is the decomposition of the substance by means of water of crystallization. A mixture of equal parts of fused sodium peroxide and crystallized sodium sulphate or carbonate, upon being gently warmed, evolves oxygen in a steady stream, under perfect control of the operator. A 10 gram piece of "oxone" readily evolves, by this process, 4 liters of oxygen. The oxygen is 99 per cent pure, perfectly odorless, tasteless and colorless.

Within the last few months calcium carbide has been decomposed by a like process, known as the Atkins system, with the production of the so-called "sun gas," which is being developed by the Sun Gas Company, of London.

HAROLD J. TURNER.

REPORTS.

Thiophosphoric Acids and Thiophosphates.

Professor Alfred Stock and his assistants in the University of Berlin, published an article recently of which the following is an abstract.[1]

Stock and Hoffmann, 3 years ago, found that phosphorus pentasulphide dissolves in liquid ammonia, forming a yellow solution which becomes colorless on standing and deposits crystals of triammonium imidotrithiophosphate, (2) while diammonium nitrilodithiophosphate, (3) remains in solution in the liquid ammonia and can be isolated by evaporation in a vacuum; the numbers in parentheses refer to the structural formulas given in the table. The authors believe that the yellow solution of phosphorus pentasulphide in ammonia contains the ammonium salt of diimidothiopyrophosphoric acid, to which they assign the constitution (1). If so, the reaction is

$$P_2S_5 + 6NH_3 = (NH)_2P_2S_5(NH_4)_4$$

and this salt reacts with ammonia as follows:

$$(NH)_2P_2S_5(NH_4)_4 + NH_3 = HNP(SNH_4)_3 + NP(SNH_4)_2.$$

From these compounds the authors have isolated a number of derivatives. The limits of a report forbid dwelling on the experimental difficulties encountered; owing to the extreme ease with which the compounds are decomposed by water the work was arduous.

The ammonium imidotrithiophosphate (2) yields several products. Treated with sodium ethylate the disodium salt (4) is formed even when a large excess of sodium ethylate is used, the presence of the imide group apparently weakening the acid; the triammonium salt also is only stable at low temperatures, breaking down, at the ordinary temperature, into ammonia and the diammonium salt.

The ammonium imidotrithiophosphate is remarkably sensitive to moisture; when shaken with ether containing 1

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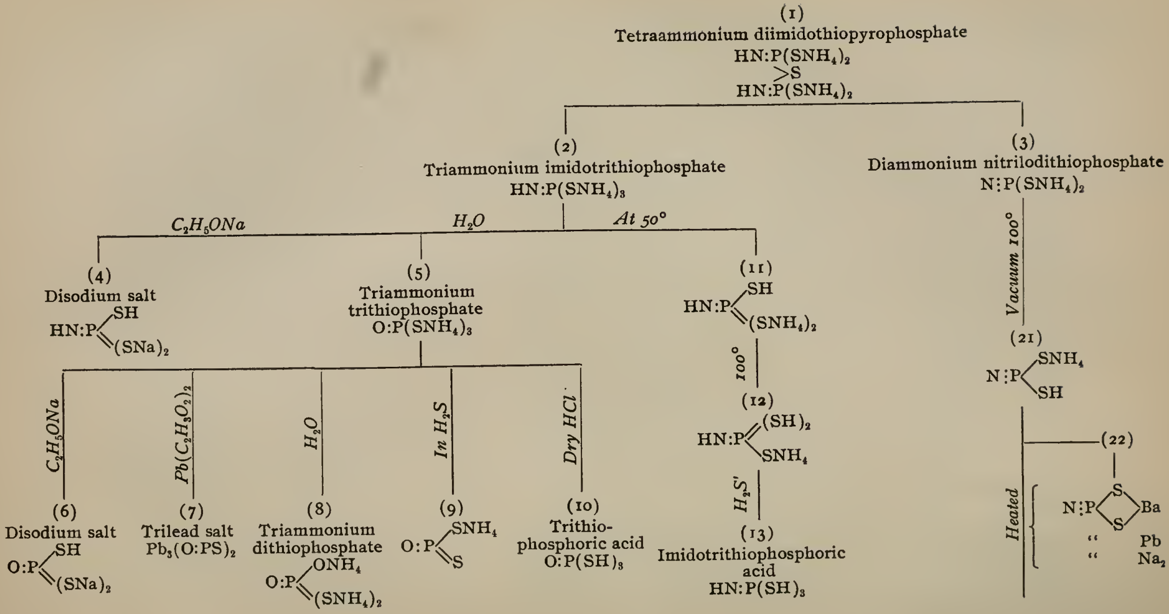
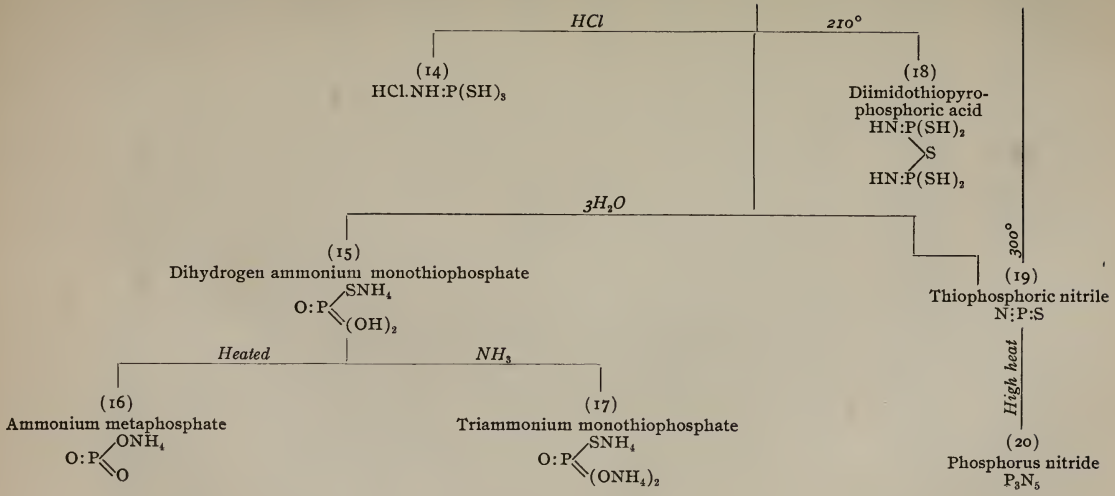
[1] Ber. d. chem. Ges., 39, 1967 (1906).


(1)
Tetraammonium diimidothiopyrophosphate
$HN:P(SNH_4)_2 >S HN:P(SNH_4)_2$
(2)
Triammonium imidotrithiophosphate
$HN:P(SNH_4)_3$
(3)
Diammonium nitrilodithiophosphate
$N:P(SNH_4)_2$
C_2H_5ONa
H_2O
At 50°
Vacuum 100°
(4)
Disodium salt
$HN:P(SH)(SNa)_2$
(5)
Triammonium
trithiophosphate
$O:P(SNH_4)_3$
(11)
$HN:P(SH)(SNH_4)_2$
100°
(12)
$HN:P(SH)_2(SNH_4)$
H_2S'
(13)
Imidotrithiophosphoric
acid
$HN:P(SH)_3$
(21)
$N:P(SNH_4)(SH)$
Heated
(22)
$N:P(S_2)Ba$
" Pb
" Na_2
C_2H_5ONa
$Pb(C_2H_3O_2)_2$
H_2O
In H_2S
Dry HCl
(6)
Disodium salt
$O:P(SH)(SNa)_2$
(7)
Trilead salt
$Pb_3(O:PS)_2$
(8)
Triammonium
dithiophosphate
$O:P(ONH_4)(SNH_4)_2$
(9)
$O:P(SNH_4)(S)$
(10)
Trithio-
phosphoric acid
$O:P(SH)_3$


HCl
210°
300°
(14)
HCl.NH:P(SH)3
(18)
Diimidothiopyrophosphoric acid
HN:P(SH)2
S
HN:P(SH)2
3H2O
(15)
Dihydrogen ammonium monothiophosphate
O:P
SNH4
(OH)2
(19)
Thiophosphoric nitrile
N:P:S
Heated
NH3
High heat
(16)
Ammonium metaphosphate
O:P
ONH4
O
(17)
Triammonium monothiophosphate
O:P
SNH4
(ONH4)2
(20)
Phosphorus nitride
P3N5

per cent of water the imide group is eliminated as ammonia, and is replaced by the oxygen of the water, forming triammonium trithiophosphate (5). Loss of the imide group strengthens the acid, for this triammonium salt does not lose ammonia at the ordinary temperature.

Triammonium trithiophosphate, treated with sodium ethylate, yields an extremely unstable disodium salt (6). A yellow trilead salt (7) and a white tricadmium salt were also made, the two latter being insoluble in water and relatively stable.

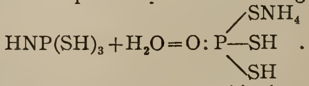
While the aqueous solution of ammonium trithiophosphate is not immediately decomposed, after standing a short time the water reacts, substituting oxygen for one sulphur atom which is thrown off as hydrogen sulphide. Triammonium dithiophosphate (8) results, which can be obtained in crystalline form by precipitation with alcohol from the aqueous solution. This substance has been already made by Kubierschky[1] by the action of phosphorus pentasulphide on aqueous ammonia; he made several salts of this acid. His work was repeated and confirmed by the present authors.

If triammonium dithiophosphate is heated in a current of hydrogen sulphide ammonium sulphide escapes and yellow ammonium dithiometaphosphate (9) is formed.

If the triammonium dithiophosphate is treated with dry, liquefied hydrogen chloride or hydrogen bromide, the free thio acid (10) is formed, but Stock did not succeed in obtaining this extremely unstable substance in a pure condition.

Returning to the triammonium imidotrithiophosphate (2), Stock found that if it were placed in a desiccator over sulphuric acid it readily loses one molecule of ammonia, forming the diammonium salt (11), which, at 100°, loses a second molecule of ammonia, forming the monammonium salt (12). When this latter salt is heated in a current of hydrogen sulphide, it loses the final molecule of ammonia and the yellow imidotrithiophosphoric acid (13) is obtained. This acid is very reactive; as an imido compound it forms, with dry hydrogen chloride, a white hydrochloride (14).

Imidothiophosphoric acid is decomposed by water forming ammonium trithiophosphate,



$$HNP(SH)_3 + H_2O = O{:}P\begin{cases} SNH_4 \\ SH \\ SH \end{cases} .$$

The decomposition continues till ammonium monothiophosphate (15) is formed, which was isolated in a condition of purity,

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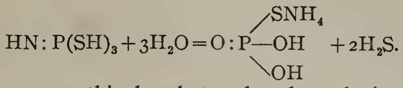
[1] J. prakt. Chem., 1885, p. 93.



$$HN:P(SH)_3 + 3H_2O = O:P\begin{array}{l} \diagup SNH_4 \\ -OH \\ \diagdown OH \end{array} + 2H_2S.$$

Ammonium monothiophosphate when heated gives off hydrogen sulphide, leaving ammonium metaphosphate (16).

Ammonium monothiophosphate, if treated with liquid ammonia, yields the tertiary salt (17) which, like the corresponding phosphate, $(NH_4)_3PO_4$, is stable only in presence of ammonia.

Stock has succeeded in isolating the triammonium salts of the 3 thiophosphoric acids (5, 8, 17).

On heating imidotrithiophosphoric acid, hydrogen sulphide escapes. Probably several successive products are formed, but their isolation is difficult; the first of these, the pyro-acid (18) was, however, separated in a nearly pure condition. It is interesting because its ammonium salt is believed to be the substance formed by dissolving phosphorus pentasulphide in liquid ammonia (1). This belief found support in the behavior of the pyro-acid towards liquid ammonia; the acid dissolved, forming a yellow solution which behaved like the substance numbered (1).

If the imidotrithiophosphoric acid is heated in a vacuum at 300° it becomes colorless and loses still more hydrogen sulphide, forming thiophosphoric nitrile, of the empirical composition NPS (19). This substance has no acid properties and is not decomposed by water. It corresponds to the known phosphoric nitrile NPO.

When the nitrile is heated to redness there remains the phosphorus nitride, P_3N_5: $5PNS = P_3N_5 + P_2S_5$.

This nitride was discovered by Stock and Hoffmann some time ago. Stock and Grüneberg are now engaged in experimenting on its direct formation from phosphorus pentasulphide and ammonia. They have observed that if phosphorus pentasulphide is treated at ordinary temperatures with dry, gaseous ammonia and gradually heated to 850°, all of the phosphorus of the pentasulphide is found as nitride. This could be expressed by the empirical equation:

$$3P_2S_5 + 10NH_3 = 2P_3N_5 + 15H_2S.$$

But few derivatives were obtained from the diammonium nitrilodithiophosphate (3). It is an amorphous, colorless substance; heated in a vacuum at 100° it loses ammonia, leaving the crystalline monammonium salt (21) from which the barium, lead and disodium salts (22) were prepared.

When the ammonium nitrilodithiophosphate is heated in a vacuum, it loses ammonia and hydrogen sulphide. Numerous attempts to isolate the free nitrilothio-acid failed. If the heat was raised to 300° the thionitrile, NPS (19), was obtained, while if red heat was employed the nitride, P_3N_5, was the endproduct.

Other sulphides of phosphorus react with liquid ammonia, but apparently in a more complicated manner.

E. RENOUF.

On a Method for Determining the Specific Heat of Solutions; Contribution to the Study of Hydrates.

In a recently published paper[1] Fuchs describes a simple and accurate method for the study of the specific heats of solutions, and shows how the hydrates existing in these solutions affect the results.

The same amount of energy was imparted at the same rate to the different solutions, by passing a measured current of electricity through a glass tube containing mercury, which was completely immersed in the liquid that was being investigated. This liquid was contained in a platinum calorimeter of 600 cc. capacity, so arranged that it might be surrounded by a constant temperature bath. The usual precautions were taken to obtain uniform temperature, and to guard against radiation.

Temperatures were read to 0°.0001. The whole apparatus was carefully calibrated, and its various heat constants determined. The solution, previously brought to room temperature, was introduced into the apparatus, the stirrer set in motion and, after a few minutes, the temperature having become constant, the thermometer was read. The circuit was closed, and after 5 minutes was interrupted. The maximum temperature reached was nearly always read after 9 minutes.

Some non-electrolytes and poor electrolytes, as well as strong electrolytes, were studied. The relation between the hydration of a dissociated substance and the temperature coefficient of its heat of neutralization, and between hydration and temperature coefficients of heat of dilution, are also taken up.

Fuchs calls attention to the hypothesis of Puschl that the water which enters into combination has a lower specific heat than that which is free, and bases part of his calculations upon it. He finds that the hydrates of dissociated substances are combinations whose stability varies with the temperature, a conclusion also previously reached by Jones from his cryoscopic work.

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[1] Dissertation, University of Nancy.

The temperature coefficient of heat of neutralization, or of heat of dilution, is a function of the hydration of the substance, in fact, is proportional to the quantity of hydration. The coefficient is positive or negative, depending upon whether there is increase or decrease in the amount of combined water.

The author concludes that the specific heat of solution may be influenced by polymerization, by ionization and by the hydrating power of the substance.

His work shows, from a consideration of specific heats of solutions, that the non-electrolytes and poor electrolytes have, in general, small hydrating power. The compounds whose aqueous solutions are good conductors, on the other hand, have a great tendency to form hydrates when dissociated. This result confirms that obtained by Jones and Bassett through cryoscopic measurements. "The hydrating tendency of the good electrolytes increases with dilution as the law of mass action would lead us to expect." This result also is confirmatory of the results obtained by Jones and his co-workers.

The neutral molecules and the ions of weak bases and weak acids, as well as the hydrogen and hydroxyl ions, according to Fuchs, hydrate much less than the anions of strong acids and the cations of strong bases. It follows, therefore, that the affinity of a substance for the solvent by which it is ionized is not the sole cause of dissociation, as Auwers and his pupils contend. As examples are cited, trichloracetic acid which does not form hydrates, and the organic ammonium salts which have very little affinity for water; the ionization of these bodies being as strong as that of the other good electrolytes.

The alcoholates are of considerable complexity, consequently, the variation of the heat of neutralization in alcoholic solutions with the temperature is large.

Fuchs also studies the conductivities of certain substances with a view to ascertaining the effect of hydration, since the weak electrolytes have little affinity for water when compared with the strong electrolytes. He finds that the ionic velocities of the weak electrolytes remain constant with change in dilution, while that of the strong electrolytes diminishes as the dilution increases. This conclusion is in accord with the results obtained by the aid of the specific heats of solutions, when the hydration is taken into account. The author attributes the failure of Ostwald's formula: $\frac{\alpha^2}{(1-\alpha)v} = C$, to hold for strong electrolytes, to the modifying effects of hydration. This follows directly from Jones' idea that the mobility of the ion depends upon the amount of water attached to it, *i. e.*, the greater the hydration the more the freedom of movement of the ion is interfered with. C. M. STINE.

REVIEWS.

ANALYSE DES MÉTAUX PAR ÉLECTROLYSE, par A. HOLLARD, Docteur ès-sciences, Chef du Laboratoire Central des Usines de la Cie Fse des Métaux, and L. BERTIAUX, essayeur du commerce. Paris: H. Dunod et E. Pinat, Éditeurs. 1906. pp. 180. Price, 6 Fr.

This work, as is stated in the preface, is not a compilation of the publications of a number of workers, but is the result of a dozen years of synthetical and analytical experiments by the authors. They have not only tested the methods synthetically, with known weights and mixtures, but have applied them to the analytical separation and detection of a variety of substances, such as minerals, alloys and commercial products. They also include in this volume an explanation of the theory of analysis by electrolysis, thus not only offering an interpretation of these complex phenomena, but also furnishing a guide for those who wish to carry on investigations in this general field. The authors have worked out a rational method of arrangement of the metals according to their behavior in determinations or separations by electrolytic methods; this, together with the principles upon which these separations are based, occupies Part I of the work. Part II contains the processes for determining the individual metals or of separating them from one another. In Part III the methods of analysis of minerals, alloys, etc., is given and in the fourth part the tables containing records of the experiments and the degree of accuracy of the determinations.

The authors have studied the conditions under which the metals can be deposited by electrolysis and have devised methods by which metals, whose properties are very similar, can be separated. They find, for example, that while zinc and cadmium cannot be separated if a platinum electrode is used, owing to the fact that the solution tension is so nearly equal, by using a cadmium cathode the tension of the hydrogen, which varies with the metal constituting the cathode, is between that of the two metals, and the one which shows the lowest tension is precipitated alone, in a strongly acid solution. They point out that while the metals cannot be classed according to the scheme followed in their qualitative separation they can be divided, according to their solution tension, into a group which can and one which cannot be deposited in a strongly acid solution. In each case all the details are given, so that there should be no difficulty in following the exact procedure recommended. Methods are described by which the different impurities in commercial metals can be determined with great accuracy by electrolytic methods. In examining this book one is impressed with the thoroughness with which the ground has been covered. Because of their accuracy and greater speed, these electrolytic processes will, without doubt, displace the older methods, especially in commercial laboratories, when time is an important factor.

J. E. G.

PREMIER CONGRÈS INTERNATIONAL POUR L'ÉTUDE DE LA RADIOLOGIE ET DE L'IONISATION; Tenu a Liége du 12 au 14 Septembre, 1905. Comptes rendus. Paris: H. Dunod et E. Pinat, Éditeurs. 1906. pp. 560. Price, $3.50.

The congress, the proceedings of which are here reported, is in some respects the most remarkable that has ever been held in connection with any scientific subject. It had to do chiefly with the subject of radioactivity in the broad sense. When it is recalled that this whole subject was first opened up only a comparatively few years ago by the discovery of the radioactivity of uranium by Becquerel, the unique character of a special conference being called to deal with radioactive problems becomes manifest.

The substance which, of course, is most important in this connection is radium, and radium was discovered only 3 or 4 years ago by the Curies. Further, the total amount of radium compounds, of a fair degree of purity, which has thus far been isolated, is a comparatively few grams.

When these two facts are taken into account, the significance of a special congress to consider the phenomena presented by this substance dawns upon us. The properties of radium and other radioactive bodies are so remarkable, and so different from those possessed by any other known substances, that although only a few grams of its salts have been isolated, it has seemed desirable to call a special meeting of physicists to discuss them.

As will be seen from the title of the "Report" the meeting was held in Liége from the 12th to the 14th of September, 1905. A large number of the leading physicists were present, and several papers of unusual interest were presented. Some of the more important are:

The increase in the conductivity of dielectrics when subjected to the action of the radium radiation, by Prof. Righi.

The analysis of the radiation of radioactive substances, by Prof. Becquerel.

A new radioactive element, radiothorium, which gives the same emanation as thorium, by Prof. Ramsay.

Some quantitative determinations of the heat evolved by radium, by Prof. Ångström.

Properties of condensation nuclei and their atmospheric distribution, by Prof. Barus.

On the ultimate disintegration products of the radioactive elements, by Prof. Boltwood.

The physiological action of radium was given considerable prominence at this congress. In this connection should be mentioned especially the papers by Prof. Dubois, Dr. Darier, Dr. Halkin and Prof. Lassar.

It should be noted that not only has a special congress been called to study the phenomena of radioactivity, but a special journal (*La Radium*) is now being published, in which the results of work in this field are being recorded. Such developments as these have no parallel in the history of Physical Science.
H. C. J.

THE ELEMENTS OF CHEMICAL ENGINEERING. By J. GROSSMAN. With a Preface by SIR WILLIAM RAMSAY. London: Chas. Griffin & Co., Ltd. Philadelphia: J. B. Lippincott Co. 1906. pp. VIII + 152. Price, $1.50 net.

In this little book the author has attempted the difficult feat of condensing, within a small volume, the elements of chemical engineering. A brief course on this subject is much needed, for few technical schools allow sufficient time in their curricula for the study of the larger works, *e. g.*, that of Davis. The author assumes that the reader has some knowledge of chemical technology (*e. g.*, *vide* p. 49). Granting this, it seems to the reviewer that there is unnecessary diffuseness of statement in many cases, though in others, clearness of expression and description have been sacrificed to brevity. Also, some of the material presented bears the impress of the kindergarten method of instruction. This last, however, may appeal to many teachers into whose hands the book will come, as the best way of awakening the interest of the student. An examination of the material presented, reveals much valuable information, especially in Chapters X and XI, upon the Materials Used in Chemical Engineering, and on the Design of Plant. The discussion of Application of Heat, and Fuel, is excellent, as far as it goes, but is all too brief. A misprint on page 33 (balls for *bells*), leads to some obscurity of meaning. With certain further additions of purely engineering topics, *e. g.*, pumps, fans, shafting, etc., the excision of verbiage and a more extended treatment of the subjects presented, a most useful book to the teacher and student will result.

F. H. THORP.

SECHS VORTRÄGE ÜBER DAS THERMODYNAMISCHE POTENTIAL, U. S. W., von J. J. VAN LAAR. Braunschweig: Vieweg und Sohn, 1906. Price, M. 3.50.

This small volume of 119 pages contains 6 lectures on the thermodynamic potential and its applications to problems of equilibrium in the fields of chemistry and physics, together with 2 lectures on concentrated solutions and on osmotic pressure. The work is of great interest and is strongly recommended to all students, especially to those working in chemistry. The volume contains little that is new, but the manner of presentation is clear and attractive. The great importance of the book comes from the attention it draws to the work of Van der Waals on the thermodynamic potential of liquids and its extension to include the case of concentrated solutions. The author emphasizes throughout the work the importance of the idea of a thermodynamic potential as introduced by Gibbs, and shows how the term osmotic pressure is limited in its usefulness and often leads to serious errors. It would be of the greatest advantage to all students of chemistry, whether in the field of physical chemistry or not, if they could receive a course of lectures based upon this work. J. S. A.

GENERAL PRINCIPLES OF ORGANIC SYNTHESES. By P. ALEXEYEFF, late Professor of Chemistry, University of Kieff. Authorized translation with revision and additions by J. MERRITT MATTHEWS, PH.D. First edition. First thousand. New York: John Wiley and Sons. London: Chapman and Hall, Limited. 1906. pp. VIII + 246. Price, $3.00.

The object and scope of this book are best set forth by the following extracts from the translator's preface: " * * * in this volume, I have made rather extensive additions of new material, together with a general rearrangement of the entire subject-matter. * * * This book is intended for the general student of advanced organic chemistry, and deals only with the theory of the subject. * * * The attempt of the author has been to present the theory of organic radicles in a systematic form and in as logical a method of development as possible, so that the student may acquire a comprehensive grasp of the general principles underlying synthetic organic chemistry." Any work which will contribute to the help of students along these lines is sure of a hearty welcome from all teachers of the subject. Unfortunately, the present volume is not of this character, and it can hardly fail to do harm to any student who reads it. This verdict is based on the following grounds: The book shows many signs of lack of careful construction and revision, and for these the translator must be responsible because Professor Alexeyeff died some years before the translation was commenced. Pages are disfigured by obvious defects in proof-reading and by lengthy foot-notes. The legitimate use of a foot-note is well understood; unfortunately they are often used by authors as a refuge from the trouble involved in welding into compact and clear form, matter which occurs to them at intervals in the course of their work, so the later idea is put in a foot-note. Now it is not fair to expect *any* reader, and least of all a student, to buy a book and then do the author's thinking for him, yet this is often necessary in the volume under consideration. One instance will suffice: The foot-note on page 3 contains an utterly erroneous statement which is wholly incompatible with one on the same subject in the text on page 5. The statement about ketones on the same page is, to say the least, very badly expressed. Two further examples of great lack of care may be given: On pages 6 and 7 a table of possible oxidation derivatives of propane is given, distinction being made between those which are known and those which have not hitherto been prepared, but the table has been quoted, *without revision*, from a book published 16 years ago! Again, camphoric acid is stated (page 21) not to be "a dibasic acid, but a compound of alcohol, ketone and acid," and its extended formula is shown on this basis. The authority for such an interesting and startling statement is a paper by Friedel, published in 1889. The amount of work done on camphor and its derivatives since that date is relatively enormous, and to ignore it in this manner is inexcusable.

A word must be added about nomenclature. It is unfortunate that the translator appears to have adopted a system of his own, but even in the use of this he is inconsistent.

Less serious defects, though by no means to be passed over, are the use of the term "amido" when "amino" is meant, and the disfigurement of the pages with a shower of hyphens which are employed incorrectly.

There are other points that invite criticism but space will not permit of their enumeration; sufficient has, perhaps, been said to show that the book should not be allowed to fall into the hands of students, whom it could only confuse and mislead, while to the more expert chemist it would hardly be useful.

The publishers have done their part well and the text betrays no very obvious signs of being a translation.

J. BISHOP TINGLE.

536

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CHEMICAL JOURNAL

Contributions from the Sheffield Laboratory of Yale University.

THE DOUBLE AMMONIUM LEAD CHLORIDES.[1]

BY H. W. FOOTE AND L. H. LEVY.

These experiments were undertaken to determine the double ammonium lead chlorides capable of forming at 25°. We used the solubility method[2] which has already been applied to several series of double salts.

André[3] described a number of double ammonium lead chlorides which were shown not to exist by Randall[4] and by Wells and Johnston[5] in papers which appeared at about the same time.

Randall described instead the 2 salts:

$$2NH_4Cl.PbCl_2$$
$$NH_4Cl.2PbCl_2$$

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[1] NOTE—Having carefully followed the work described in this article, and having compared the products obtained with our original sample of the supposed salt $NH_4Cl.PbCl_2.H_2O$ made by Wells and Johnston, I am fully convinced that the latter was not a pure product, but $NH_4Cl.2PbCl_2$ contaminated with ammonium chloride and mother liquor. The molecular weight of NH_4Cl is so small in comparison with that of $PbCl_2$ that a moderate amount of such contamination led to mistaken conclusions.
H. L. WELLS.

[2] THIS JOURNAL, **30**, 330 (1903).

[3] Compt. rend., **96**, 435 (1883).

[4] THIS JOURNAL, **15**, 494 (1893).

[5] Am. J. Sci., **46**, 25 (1893).

and Wells and Johnston the salts:

$NH_4Cl.PbCl_2.H_2O.$
$NH_4Cl.2PbCl_2.$

It will be noticed that the 1 : 2 salt was found by both Randall and Wells and Johnston, but there is a disagreement in regard to the other 2 salts.

In our experiments, weighed quantities of ammonium chloride and lead chloride were treated with a known quantity of water, the mixtures heated and then allowed to crystallize. They were shaken, usually for several days, in the thermostat, at 25°. At the ammonium end of the series, the mixed salts were entirely dissolved when heated. At the lead end this could not be done, but the thorough shaking insured equilibrium. Both solutions and residues were analyzed. The solutions were drawn into a pipette, through a filter of glass wool and weighed. The pipette was first warmed slightly to prevent crystallization on the walls. The residue in the bottles was removed as quickly as possible and dried between filter paper. Ammonia was determined by distilling with sodium hydroxide and passing the distillate into a known amount of standard hydrochloric acid. The excess of acid was titrated by means of a standard solution of ammonia. Lead was determined by adding a little nitric acid, to dissolve all lead chloride, and then 10 cc. of sulphuric acid, the solution being subsequently evaporated on a steam-bath to sulphuric acid. The lead sulphate, after treating with a small amount of water, was filtered on a Gooch crucible, washed with a very dilute solution of sulphuric acid, ignited and weighed. The results of the analyses of both solutions and residues follow:

Table I.—Solubility of Ammonium and Lead Chlorides at 25°.

	Per cent NH_4Cl in sol.	Per cent $PbCl_2$ in sol.	Per cent NH_4Cl in res.	Per cent $PbCl_2$ in res.	Composition of residue.
1.	28.41	1.17	95.06	3.22	$NH_4Cl + NH_4Cl.2PbCl_2$
2.	27.89	1.22	50.80	47.70	" "
3.	27.71	0.99	12.30	87.04	" "
4.	*27.45*	*0.93*	*10.27*	*88.61*	$NH_4Cl.2PbCl_2$
5.	*26.25*	*0.75*	*10.24*	*89.04*	"

Table I—(continued).

	Per cent NH_4Cl in sol.	Per cent $PbCl_2$ in sol.	Per cent NH_4Cl in res.	Per cent $PbCl_2$ in res.	Composition of residue.
6.	*24.69*	*0.85*	*10.46*	*88.74*	$NH_4Cl.2PbCl_2$
7.	*21.59*	*0.35*	*10.56*	*88.42*	"
8.	*17.97*	*0.29*	*9.62*	*89.92*	"
9.	*13.51*	*0.17*	*8.93*	*90.76*	"
10.	*11.47*	*0.12*	*8.71*	*90.88*	"
11.	*10.25*	*0.11*	*8.52*	*91.20*	"
	Calculated,		8.78	91.22	
12.	2.71	0.06	7.30	92.60	$NH_4Cl.2PbCl_2 + PbCl_2$
13.	2.81	0.04	7.24	92.70	" "
14.	2.78	0.01	5.87	93.72	" "
15.	2.79	0.02	1.51	98.22	" "

These solubility results are not entirely satisfactory in every respect, but they prove certain points. In Nos. 1–3 the solubility remains practically constant, showing that the same salts are present in the residue. As the residues vary from 95.06–12.30 per cent of ammonium chloride, it is evident that the 2 : 1 salt and the 1 : 1 : 1 could not have formed, as the latter contains 15.32 per cent of ammonium chloride. Had either of these formed, the solubility results in Nos. 1 and 2 would have differed from No. 3. In these experiments, there was evidently a mixture of ammonium chloride and a double salt containing less than 12 per cent of ammonium chloride.

Experiments 12–15 also have constant solubility and show that mixtures were present containing lead chloride and a double salt with more than 7.3 per cent of ammonium chloride.

Nos. 4–11 show widely varying solubility, indicating the presence of a pure double salt, but the residues are not constant in composition, varying from 10.27 to 8.52 per cent of ammonium chloride.

We were at first inclined to believe from the results that 2 salts were present, the 1 : 2, which was described before, and also a salt having the composition $3NH_4Cl.5PbCl_2$. The latter salt would contain 10.36 per cent of ammonium chloride. Subsequent results showed that but one salt was present.

The residues were always very fine and it was not easy to dry them rapidly between filter paper. Any mother liquor drying on the salt would tend to increase the percentage of ammonium chloride in the residue, and this would be more noticeable when the solutions were at the ammonium end of the series. The crystals may have also included a small amount of mother liquor, which would tend to increase the percentage of ammonium chloride found.

In deciding what salt was present in Experiments 4–11 of the preceding table, we proceeded as follows: Two solutions were prepared from calculated amounts of ammonium chloride, lead chloride and water, so that a small quantity of crystals would separate at 25° from one solution near the ammonium end of the series and from the other solution near the lead end. The necessary charges were calculated from the solubility results previously given. The quantities of salts and water used were the following:

I. Ammonium end.			II. Lead end.		
501	grams	NH_4Cl	160	grams	NH_4Cl
25.86	"	$PbCl_2$	6.56	"	$PbCl_2$
1483	cc.	H_2O	1838	cc.	H_2O

The salts were completely dissolved in the water by heating the mixtures. The solutions were placed in a thermostat at 25° and allowed to crystallize. The crystals from solution I were larger than those from solution II. Some of them from each solution were examined by Professor S. L. Penfield a few months before his death. The crystals were not sufficiently well formed to allow of accurate optical measurements. They both, however, were similar in form and habit and had identical optical properties, so far as these could be distinguished, so that the same salt was evidently present in each case.

For analysis, the crystals were removed from the solutions and dried rapidly between filter paper. The same methods of determination were used as before. The following results were obtained:

	I.	II.	Calculated for $NH_4Cl.2PbCl_2$.	Calculated for $3NH_4Cl.5PbCl_2$
$PbCl_2$	90.09 ; 89.94 ; 89.96	90.50	91.22	89.64
NH_4Cl	. . . . . .	9.68 ; 9.67	8.78	10.36

The results are not as close as could be desired, coming between the theoretical percentages for the 1:2 and the 3:5. As the solutions contained a large excess of ammonium chloride, the ammonium would tend to come high in the analyses and the lead correspondingly low, so there can be no doubt that the salt present in each case was $NH_4Cl.2PbCl_2$, which has previously been described.

An attempt was now made to prepare the 2:1 salt according to Randall's directions. Two hundred and fifty cc. of ammonium chloride solution, saturated in the cold, were raised to the boiling point and 15 grams of lead chloride added. This did not all dissolve and 50 cc. of ammonium chloride were added and the solution heated, after which the solution cleared. The beaker, containing this solution, was set aside to cool, by placing it within another beaker and surrounding it with cotton waste. After some days the beaker was removed and 2 layers of crystals were noticed. Portions of both these layers were removed and ammonia determined. The results were:

	Per cent NH_4Cl.
Upper layer	65.35
Lower layer	20.78
Calculated for 2 : 1 salt	27.82

Experiments were also carried on to ascertain if another double salt formed at a different temperature. A mixture of the 1:2 salt and ammonium chloride was placed in a dilatometer and readings taken from 0°–70°, but no irregular change in volume was observed, making it very probable that only the one double salt forms in the range of temperature investigated.

SHEFFIELD LABORATORY,
NEW HAVEN, CONN.,
October, 1906.

Contributions from the Sheffield Laboratory of Yale University.

THE DOUBLE CAESIUM LEAD BROMIDES.

BY H. W. FOOTE.

The double caesium lead bromides have been described by Wells and Walden.[1] They are the following:

$CsPb_2Br_5$

$CsPbBr_3$

Cs_4PbBr_6.

The salt $CsPbBr_3$ was described as occurring in 2 different forms, one white and the other orange-colored. The white form passed into the orange when heated, but the reverse change did not take place upon cooling. The orange form was prepared under a wide range of conditions, while the white form was obtained only from solutions containing but little caesium bromide.

In the present article, the conditions of formation of the 3 salts have been determined at 25°, by the solubility method, chiefly with the object of ascertaining whether or not both forms of the 1 : 1 salt could be obtained at this temperature by varying the proportions of caesium and lead bromides in solution. Only the orange form could be isolated, however, and the white form is, apparently, unstable at this temperature.

Lead bromide was prepared by precipitating a solution of lead nitrate with pure hydrobromic acid; caesium bromide, by dissolving very pure caesium carbonate in hydrobromic acid and evaporating to dryness.

The experiments were carried out as described in the preceding article. As it was feared that lead bromide might hydrolyze and form a basic bromide, a very dilute solution of hydrobromic acid was used as solvent instead of pure water. This solution contained 0.1906 gram of hydrobromic acid in 25 cc.

Solutions and residues were analyzed by dissolving in water with the addition of nitric acid, when necessary to complete the solution, adding a slight excess of sulphuric acid and evaporating till water was removed. The residue was treated with a tle water, and lead sulphate filtered on a Gooch crucible when it was present in appreciable amount. The solutions usually contained too small an amount of lead to weigh. The solution containing caesium sulphate and sulphuric acid was evaporated and heated and the normal sulphate obtained by igniting several times gently with ammonium carbonate. As the residues were anhydrous, lead alone was determined in most cases and caesium calculated by difference.

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[1] Am. J. Sci., 45, 121 (1893).

The results obtained are given in Table I. Italics are used when a double salt was present, as shown by varying solubility and constant composition of the residue.

Table I.—Solubility of Caesium Lead Bromides at 25°.

No.	Per cent CsBr in solution.	Per cent $PbBr_2$ in solution.	Per cent CsBr in residue.	Residue contains:
1.	0.24	0.33	6.62	$PbBr_2$ and $CsPb_2Br_5$
2.	0.33	0.36	18.93	
3.	*12.83*	trace	*23.50*	$CsPb_2Br_5$
4.	*17.24*	“	*22.94*	
Calculated for $CsPb_2Br_5$			22.49	
5.	17.68	trace	27.57	$CsPb_2Br_5$ and $CsPbBr_3$
6.	17.82	“	31.72	
7.	*18.58*	“	*36.21*	$CsPbBr_3$
8.	*19.57*	“	*36.51*	
9.	*33.65*	“	*37.89*	
Calculated for $CsPbBr_3$			36.72	
10.	36.53	trace	38.00	$CsPbBr_3$ and Cs_4PbBr_6
11.	36.57	“	39.80	
12.	37.18	“	48.37	
13.	36.89	“	65.54	
14.	*46.40*	“	*70.58*	Cs_4PbBr_6
15.	*51.15*	“	*70.27*	
Calculated for Cs_4PbBr_6			69.89	
16.	54.71	trace	74.92	Cs_4PbBr_6 and CsBr
17.	54.16	“	98.41	
18.	55.23	none	100	CsBr

The residues in Nos. 7–9 were deep orange, while the mixtures on either side were lighter in color, due to the presence of the other salts. The white form of this salt was never observed and it would appear to be unstable at this temperature.

The residues in Nos. 14–15 were light salmon in color instead of white. That this is the natural color of the 4 : 1 salt instead of being due to the presence of a trace of the 1 : 1 was shown by the fact that the mixture of this salt with caesium bromide was also slightly colored.

SHEFFIELD LABORATORY,
NEW HAVEN, CONN.,
October, 1906.

THE ABSORPTION SPECTRA OF CERTAIN SALTS IN AQUEOUS SOLUTION AS AFFECTED BY THE PRESENCE OF CERTAIN OTHER SALTS WITH LARGE HYDRATING POWER.

BY HARRY C. JONES AND HORACE S. UHLER.

(SEVENTEENTH COMMUNICATION.)

[This investigation was carried out with the aid of a grant from the Carnegie Institution.]

The importance of the absorption spectra of salts as affected by the presence of certain other salts, in their bearing on the hydrate theory as proposed hy Jones, has already been pointed out.[1] It has been mentioned that our attention was directed to certain of these color changes by Dr. Lewis.

The chief reactions that we have studied are those between cobalt chloride, copper chloride and copper bromide, when treated with calcium chloride, calcium bromide, or aluminium chloride. It is well known that aqueous solutions of cobalt chloride are purplish-red in color. When a strong, aqueous solution of cobalt chloride is treated with a fairly concentrated, aqueous solution of calcium chloride, the color of the cobalt solution is changed from purplish-red to blue. This same result is obtained if calcium bromide is used instead of calcium chloride.

Similar color changes result when solutions of aluminium chloride are added to solutions of cobalt chloride. Indeed, smaller amounts of aluminium chloride are required to affect the same color changes, than are necessary when either of the salts of calcium is used.

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[1] THIS JOURNAL, **34**, 291 (1905). J. Chim. physik., 3, 494 (1905).

If any one of the above-named dehydrating agents is added to a fairly dilute solution of cupric chloride or bromide, marked color changes result. A fairly concentrated solution of cupric chloride or bromide is greenish-brown, while dilute solutions are blue. As more and more water is added to the more concentrated solutions, we have all gradations between the above colors. The addition of calcium chloride, calcium bromide, or aluminium chloride to a blue solution of the copper salt, changes the color to green, and if sufficient of the dehydrating agent is added the color becomes greenish-brown.

In the present investigation these color changes have been studied quantitatively. The absorption spectra of the substances separately, and when mixed in known quantities, have been observed by means of a direct-reading spectroscope, and the wave lengths of the absorption bands read off and recorded.

What is of far greater importance, however, is the photographic record of such absorption bands, and the changes in the position of these bands as varying amounts of one or another dehydrating agent is added to the salt in question. These photographs have been taken by means of the spectrograph to be described later in this paper.

Before taking up in detail the work which is here recorded, a brief discussion of some of the more important investigations in this same field seems desirable.

The fact that dehydrating agents produce the change in color from purplish-red to blue, and, further, that the same color change is effected by raising the temperature of the solution, early suggested the view that the change in color from reddish to blue was due to a loss of water on the part of the salt in solution.

Babo[1] observed that cobalt chloride, in concentrated solution, was colored blue by absolute alcohol, at ordinary temperatures. At more elevated temperatures a few drops of alcohol are sufficient to produce the blue color. A solution of calcium chloride or magnesium chloride changes the color of cobalt chloride to blue very readily, especially at the boiling points of the solutions. A saturated solution of sodium chloride will also produce the blue color at elevated temperatures.

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[1] Ber über d. Verhand. d. Gesell. f. Beford. d. Naturw. zu Freiburg, i. B. 1857, Nr. 17, 283. Jahres. d. Chem., 1857, 72.

A concentrated solution of zinc chloride, on the other hand, gives only a red color with cobalt chloride, even when the mixture is warm. Babo thinks that this is due to the formation of a double salt. He concludes that whenever there is a transformation from the reddish to the blue color, there is a dehydration of the cobalt salt.

Gladstone,[1] in his well-known paper "On the Use of the Prism in Qualitative Analysis," takes up the question here under discussion. In connection with salts of cobalt he says: "We are accustomed to speak of blue and red salts of cobalt, but this difference depends really on the state of hydration, and the prism reveals an analogy otherwise unsuspected between the two colors."

Gladstone points out that the salts of cobalt, in general, when anhydrous, are blue, and that the hydrated salts or aqueous solutions are red. The only exception seems to be the sulphocyanate, whose saturated aqueous solution is blue. The dilute aqueous solution of even this salt is, however, red.

Gladstone,[2] in his subsequent investigations with the *isoscope*, comes essentially to the same conclusions as those pointed out above. He brought within the scope of this investigation a large number of colored compounds. Among the substances where the character of the color changes with the dilution, are the 3 salts upon which special stress has been laid in this investigation—cobalt chloride, copper chloride and copper bromide.

In 1859 Schiff[3] published a paper on the "Effect of Rise in Temperature on the Intensity of the Color of Solutions," in which such questions as those now under consideration were discussed. He added a number of cases of color changes with change of temperature to those already observed by Babo and Gladstone, and seems to be of the same general opinion as to their cause—that there is a change in the magnitude of the hydration.

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[1] J. Chem. Soc., **10**, 79 (1858).

[2] *Ibid.*, **11**, 36 (1859).

[3] Ann. Chem. (Liebig), **110**, 203 (1859).

Bersch,[1] in 1867, proposed a new view to account for the color changes in the case of cobalt salts. He recognized that when $CoCl_2.6H_2O$ is heated it yields two well-defined compounds, $CoCl_2.4H_2O$ and $CoCl_2.2H_2O$, the former being bluish-red and the latter violet in color.

He, however, thought that he established the fact that the compound $CoCl_2.6H_2O$ may become blue without loss of water. He concluded, therefore, that there are two modifications of the compound $CoCl_2.6H_2O$—the one red and the other blue—and that the first change in color on heating is due to the transformation of the red into the blue modification.

Tichborne[2] called attention to an interesting and important fact which is stated in his own words: "It is easy to portend that although impossible at ordinary atmospheric pressure, and in an ordinary aqueous solution, to dissociate the water, it is only necessary to boil such a solution under sufficient amount of pressure to obtain the thermoanalytic point. This was demonstrated by the following experiment: A weak solution of chloride of cobalt was sealed up in a glass tube, two-thirds of the capacity of which was empty. On boiling the liquid in this tube the solution gradually passes with the increment of heat through all the shades of purple, until the contents ultimately become pure blue. Thus, in this aqueous solution we have attained, by extraordinary pressure, the temperature necessary for the separation of the water. The change of color may be easily observed as it occurs in the capillary tube, by holding any white material at the back of the tube and opposite the experimenter." It is obvious that this observation is of importance in connection with the theory as to the cause of these color changes.

Attention was again called to this same fact by Clowes[3] about 2 years later.

The spectrum of cobalt chloride was early studied, especially by Vogel.[4] He pointed out that the red, aqueous solution of cobalt chloride shows only one broad band in the green, and this lies between F and D. In stronger solutions there is absorption of the violet, blue and green, only the region to the right of these being transparent.

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[1] Sitzung. Wien., II, **56**, 726 (1867).

[2] Chem. News, **25**, 133 (1872).

[3] *Ibid.*, **29**, 161 (1874).

[4] Ber. d. chem. Ges., **11**, 913 (1878).

When the solution of cobalt chloride is evaporated nearly to dryness it becomes blue. The absorption of the blue and green completely disappears, and 2 sharp bands manifest themselves in the red and orange. Vogel also studied the spectrum of the blue, alcoholic solution, and pointed out certain relations between it and the spectrum of the blue, aqueous solution. He observed, however, that the absorption bands are closer to the red in the aqueous than in the alcoholic solution.

Russell[1] made a fairly extended spectroscopic study of solutions of cobalt chloride. He worked with a fused salt, with its solution in concentrated hydrochloric acid, and with its solution in various alcohols. He showed that the spectrum in the concentrated acid was very similar to that of the fused salt, the two bands being shifted a little towards the blue. The spectrum of cobalt chloride, when dissolved in the various alcohols and in glycerin, was practically the same, independent of the nature of the solvent.

Russell also worked with aqueous solutions at different concentrations and studied their absorption spectra. He likewise studied the effect of change of temperature on the various aqueous solutions. He concluded that the color of the aqueous solutions was due to the presence of hydrates in these solutions.

Potilitzin[2] took up the study of cobalt chloride especially to test the conclusions reached by Bersch—that there are 2 modifications of the compound $CoCl_2.6H_2O$, the one red and the other blue.

Potilitzin showed that when the hexahydrate is warmed to about 52°, for 4 hours, it passes over into the dihydrate, $CoCl_2.2H_2O$, which is reddish, with a slightly violet tint. The same compound is obtained when the hexahydrate is placed in a desiccator for a few days. At 100° the dihydrate passes over into the monohydrate, $CoCl_2.H_2O$, which is dark violet in color.

[1] P. Roy. Soc., **32**, 258 (1881).

[2] Ber. d. chem. Ges., **17**, 276 (1884).

When the monohydrate is warmed from 110°–120°, it loses its last molecule of water and yields the anhydrous salt, which is blue.

Potilitzin concludes that the transition temperatures from one hydrate to another of cobalt chloride, as given by Bersch, are in error; that there is only one modification of the compound $CoCl_2.2H_2O$, and that the only other hydrate of cobalt chloride has the composition $CoCl_2.H_2O$.

The formation of blue cobalt chloride from red, by whatever means affected, is a dehydration process.

Sabatier[1] showed that hydrates of cobalt chloride containing less water than the hexahydrate, were formed when hydrochloric acid was added to a strong, aqueous solution of the cobalt salt. There seems to be some evidence of the formation of chlorhydrates.

He[2] performed similar experiments with copper chloride, and obtained analogous results.

In 1890 Lescoeur[3] took up a study of the hydrates formed by cobalt chloride. He found also that at 120° the compound $CoCl_2.2H_2O$ is produced. When any of the hydrates are heated up to 140° they yield the anhydrous chloride. The compound $CoCl_2.2H_2O$, of lilac color, is easily obtained by drying the hexahydrate over sulphuric acid, at the ordinary temperature. There is no intermediate hydrate such as $CoCl_2.4H_2O$ formed.

In 1891 a number of papers appeared bearing upon the problem under discussion. Étard[4] pointed out the importance of studying simultaneously the color changes and solubility curve. He worked with cobalt chloride and cobalt iodide, and showed that at those temperatures corresponding to the formation of a new hydrate the solubility curve changed direction, being no longer a straight line. The new hydrate would have a different solubility from the old, and this was clearly shown by the solubility curves. He thus proved the existence of the following hydrates:

$CoI_2.6H_2O$, $CoI_2.4H_2O$, $CoI_2.2H_2O$, $CoCl_2.6H_2O$, $CoCl_2.2H_2O$.

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[1] Compt. rend., **107**, 42 (1888).

[2] *Ibid.*, **106**, 1724 (1888).

[3] Ann. Chim. Phys. [6], **19**, 547 (1890).

[4] Compt. rend., **113**, 699 (1891).

Potilitzin[1] came back to the problem of the change in the color of cobalt chloride, having published a paper 7 years earlier on this same subject. He points out that when crystals of $CoCl_2.6H_2O$ melt they form a deep violet colored liquid, which becomes more and more deeply blue. He also states that dehydrating substances, in general, produce the blue color. He concludes that these changes in color are due entirely to changes in the hydration of the cobalt chloride.

Charpy[2] studied the vapor-tension of solutions of cobalt chloride and plotted the results as curves. He found that the curve was made up of two well-defined, rectilinear portions. The two portions of the curves met at 75°. Above this temperature the solutions were blue in color.

This agrees, in a sense, with the results found by Étard. As Charpy points out, his results can be interpreted in either of two ways. There is either a change in the hydration of the salt with change in temperature, or there is a change in the state of molecular aggregation. From these results it is impossible to decide between the above two possibilities.

Wyrouboff[3] calls attention to the fact that the change in the color of solutions of cobalt chloride with rise in temperature, cannot be due to the presence of the anhydrous salt, since this combines with water with the greatest avidity, a large amount of heat being at the same time liberated. He showed that the change in color was due to the formation of the monohydrate, $CoCl_2.H_2O$, which is formed in larger and larger quantities the more elevated the temperature. This violet-colored hydrate is stable, not losing its molecule of water until a temperature of 140° is reached, when it passes over into the pale blue, anhydrous salt.

Engel[4] does not accept any of the theories that have been advanced to account for the color changes that take place in cobalt chloride. He reviews briefly our knowledge of the hydrates of cobalt chloride, and then takes up the theories that have been proposed to account for the color changes.

[1] Bull. Soc. Chim. [3], **6**, 264 (1891).

[2] Compt. rend., **113**, 794 (1901).

[3] Bull. Soc. Chim. [3], **5**, 460 (1891).

[4] *Ibid.* [3], **6**, 239 (1891).

He objects to the dehydration theory, that the blue color is due to the presence of the anhydrous salt, since this salt is light blue, while the solutions are much deeper blue, and, indeed, often indigo-blue. He objects to the theory of Wyrouboff, since the monohydrate is violet and never blue, and the solutions are often blue.

Engel does not believe that any general theory can be advanced to account for the changes in color which cobalt chloride undergoes. He thinks that each special case must be dealt with separately. He is of the opinion that the blue color is due to the presence of compounds which cobalt chloride is capable of forming with various substances. Some of these compounds are not blue, notably the one formed with zinc chloride; mercuric chloride, stannous chloride and the chloride of antimony behaved like the chloride of zinc.

Engel supports his theory that the blue color is due to the presence of double chlorides, by stating that he has obtained a double chloride of calcium and cobalt and calls attention to the fact that Chassevent[1] has prepared a blue double chloride of cobalt and lithium having the composition, $CoCl_2.LiCl.3H_2O$, which is probably analogous to $CoCl_2.HCl.3H_2O$, the compound formed with hydrochloric acid. The double copper salt is, however, red. Engel thinks that the blue color produced in a saturated solution by rise in temperature, is not due solely to the presence of the monohydrate, which is violet, but to the formation of a compound with hydrochloric acid, the hydrochloric acid being liberated as the result of the action of water on cobalt chloride.

Wyrouboff[1] answers a number of the objections advanced by Engel against the dehydration theory, especially concerning the color of the monohydrate. It is largely a question of physical state, whether we are dealing with transmitted or reflected light.

Le Chatelier[2] does not doubt the existence of blue double salts—chlorhydrates, alcoholates, etc.—but thinks the color changes can be easily explained on the dehydration theory.

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[1] Bull. Soc. Chim. [3], 6, 3 (1891).

[2] *Ibid.* [3], 6, 3 (1891).

He points out that the formation of the acid chloride would involve also the formation of the oxychloride, which would be precipitated, and this is not the case.

Le Chatelier[1] shows that both red and blue cobalt chloride act on calcium carbonate, and that this and other lines of evidence adduced by Engel against the dehydrated theory are not valid.

Étard[2] studied the changes in the absorption spectra of cobalt chloride with change in temperature, and found, with rise in temperature, the disappearance of certain bands and the appearance of others. This work is analogous to that of Becquerel,[3] which deals especially with the absorption spectra of salts of didymium and uranium.

As Étard points out, the appearance of the new bands with rise in temperature shows that there is some new internal arrangement of the molecules, as we should expect if there was a change in the hydration as the temperature varies. As the nature of the molecules in the solution changes, new absorption bands will make their appearance.

The most elaborate work by far which has been done on the absorption spectra of cobalt salts is that of Hartley.[4] This is but part of an extensive investigation on the absorption spectra of a number of colored salts. The work includes also the chloride and bromide of copper.

The spectra of an aqueous solution of cobalt chloride, at temperatures ranging from 23° to 93°, were photographed and the bands also measured. Hartley concludes that his photographs of these spectra of the solution at different temperatures, show that the molecules of water are removed from the cobalt chloride with rise in temperature. The absorption bands widen in the red with rise in temperature, showing that the molecule is becoming simpler and vibrates in resonance with a larger number of waves.

Hartley worked also with solutions of cobalt chloride in absolute alcohol, at different temperatures, and concluded that

[1] Bul. Soc. Chim. [3], **6**, 84 (1891).

[2] Compt. rend., **120**, 1057 (1895).

[3] Ann. Chim. Phys. [6], **14**, 170 and 257.

[4] T. Roy. Soc. Dublin, II, **7**, 253 (1900).

rise in temperature did not affect the alcoholic solutions. He also worked with solutions of cobalt chloride in glycerin, with cobalt chloride mixed with hydrochloric acid, and with cobalt chloride to which a solution of calcium chloride had been added. Work similar to the above was done with cobalt bromide and iodide.

The effect of rise in temperature on the absorption spectra of a number of salts of chromium was also studied.

Hartley concludes that the effect of rise in temperature, in general, on the absorption spectra of solutions of salts is as follows: If the salts are anhydrous or not dehydrated at 100°, or if they do not change color when dehydrated, they do not change their absorption spectra when heated. Hydrated salts change their spectra with change in temperature, and this change is usually very nearly the same as that effected by dehydrating agents.

Ostwald[1] concludes that the red color of solutions of cobalt salts, in general, is due to the cobalt ion. He points out that the hexahydrate easily loses water and forms lower hydrates, which are blue in color. If the concentrated aqueous solutions are heated they turn blue. This same color change is very easily produced by adding to the solution of cobalt chloride chlorine ions. Thus the presence of hydrochloric acid or sodium chloride easily produces the blue color. Ostwald concludes that the blue color is due to the driving back of the dissociation of the cobalt chloride, the anhydrous salt being blue.

In a recent paper Donnan and Bassett[2] take the view that none of the theories thus far proposed is satisfactory. They make the suggestion that the blue color may be due to the presence of complex cobalt anions. They point out that the blue alcoholic solutions, when cooled down to —79°, become red, and conclude that this cannot be due to hydration. The question arises as to whether it may not be due to alcoholation.

The action of salts of zinc, mercury, cadmium, antimony and tin, in turning blue solutions of cobalt chloride red, is explained as being due to the fact that these metals have a greater tendency to form complex negative ions than cobalt, and that they therefore break up the complex ions formed by the cobalt. This explanation seems decidedly forced. Evidence of a very direct kind should certainly be furnished that the above metals do have a very great tendency to form complex anions. In some of the above cases this is certainly not obvious.

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[1] Grundlinien d. anorgan. Chem., p. 620.

[2] J. Chem. Soc., 81, 942 (1902).

Hartley[1] calls attention to some inaccuracies in the above paper. It is not at all certain that when hydrochloric acid is added to a solution of cobalt chloride the blue color is due to the same cause as when an aqueous solution is heated. Indeed, the absorption spectra in the two cases are quite different. Hartley points out, further, that the color of hot aqueous solutions was not supposed to be due to the anhydrous cobalt chloride, but to a dihydrate. Again, the spectra of a solution of cobalt chloride, saturated at 20°, and taken at the temperatures 23°, 33°, 43°, 53°, 73° and 93° are all different from the spectrum obtained from the anhydrous salt in absolute alcohol, and are also different from the cobalt chloride to which hydrochloric acid had been added.

Hartley also criticizes certain other points in the paper by Donnan and Bassett, but it would lead us too far to discuss these in detail.

Quite recently Lewis[2] has called attention to the importance of these color changes for the theory of hydrates in solution.

Jones and Bassett[3] have discussed the reactions described by Lewis, and Jones[4] has supplemented them by a number of other cases which bear directly upon the hydrate problem.

We shall now take up the work which we have carried out on the problem in hand.

APPARATUS.

The Spectrograph.—The apparatus was designed by one[5] of us in his previous study of the absorption spectra of the aniline dyes. Since reference to earlier descriptions of the spectrograph may not be convenient, a brief account of its chief characteristics will be given below. The essential parts of a vertical section of the spectrograph are outlined in their exact relative proportions in Fig. 1., which is 1/15th of the natural size. This may be described as follows: In the first place each element of the system was adjustable in every respect. Light from a Nernst filament, N, was focused by the concave speculum mirror R, on the slit S, whence it continued to the grating G, from which a portion of it was disbursed in the direction of the sensitized film, F. The adjustable support of the mirror was rigidily attached to the main body of the spectrograph. The distances from the middle of the slit to the centres of the mirror and grating were, respectively, about 89.5 and 97.1 cm. The electrodes, E, were so located above the slit, as not to interfere with the passage of light from the reflector to the slit. No lenses or other reflectors were used. The micrometer head at M indicated the separation of the slit-jaws.

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[1] J. Chem. Soc., **83**, 401 (1903).

[2] Z. physik. Chem., **52**, 222 (1905).

[3] This Journal, **34**, 291 (1905).

[4] J. chim. Phys., **3**, 455 (1905).

[5] Uhler and Wood: Monograph, Carnegie Institution.

Q and Q′ denote a screen system, such that when Q was vertical the passage of light from the grating to the camera was not interfered with, whereas when Q was horizontal only ultra-violet light of shorter wave-lengths than 0.4 μ could reach the photographic film. PP is a horizontal platform with a scale along its front edge. By sliding horizontal opaque screens of various widths along this platform, it was possible to cut out completely any region or regions of wave lengths desired. In making certain tests the platform and sliding screens were very convenient. L is the section of a thin, black, metal shutter, capable of motion in a horizontal direction, and hence at right angles to the length of the photographic films or plates. In other words, parallel to the slit and to the rulings of the grating. A number of long, rectangular slots or openings, suitably spaced and proportioned, were present in this screen, so that strips of different widths of the films or plates could be exposed to the light from the grating, without causing any displacement of the sensitized surfaces with reference to the grating and slit. This was

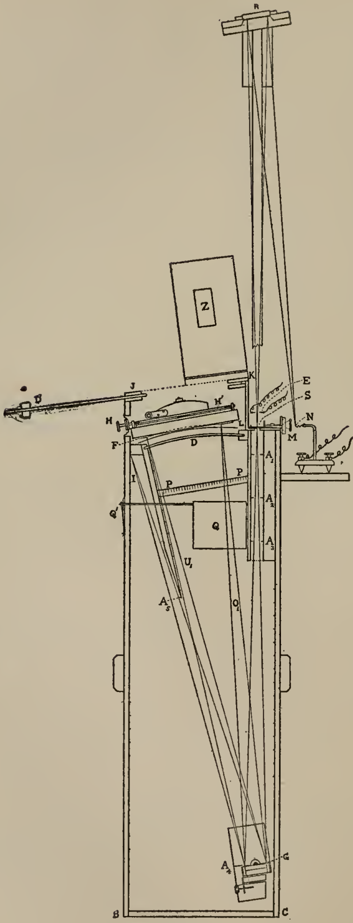

Fig. 1.

necessary for impressing comparison spectra, etc. H and H′ suggest the rack and pinion system, by the aid of which the films could have unexposed portions brought successively opposite to some selected opening in the slide screen L. D and D′ denote two of the four doors which gave access to the interior of the spectrograph, and which made it possible to close up the camera light-tight, while making various adjustments with the rest of the system. The camera was so made that when neither a film or plate was in position, it was possible for the experimenter to look directly at the grating and to make qualitative observations with the assistance of any eye-piece. Certain black-on-white scales and ruby glass windows (Z, for example) enabled the experimenter to know the precise relative positions of the various accessories in the interior of the spectrograph, when the entire system was shut up and exposures were being made. Numerous dull black diaphragms and screens (A_1, A_2, A_3, A_4, A_5, etc.,) protected the photographic film from the unusable light which came from the central image I, and from all the spectra except the one desired. U_1 and O_1 gave the extreme rays of so much of the first order spectrum as was studied photographically, that is, U_1 and O_1 correspond, respectively, to about $0.20\ \mu$ and $0.63\ \mu$. The spectrograph was, of course, dull black both inside and out, and contained plaited black velvet wherever needed. A general idea of the size of this apparatus may be derived from the following dimensions. From R to the plane of BC = 198.5 cm.; BC = 34.5 cm.; the bottom edge perpendicular to BC = 27.5 cm.; BJ = 116 cm., and JK = 29 cm.

The Spectroscope.—This instrument was of the direct-reading type, and was obtained from Hilger of London. An orthagonal projection of this spectroscope on a horizontal plane is shown at H in Fig. II. Two details of the spectroscope deserve special mention. In the first place the instrument was so designed that when the prism was properly adjusted on its turn table, and the cross-hairs were correctly placed in the telescope, the wave length of any visible spectral line which appeared to be bisected by the point of intersection of the cross-hairs could be read off directly from the graduated

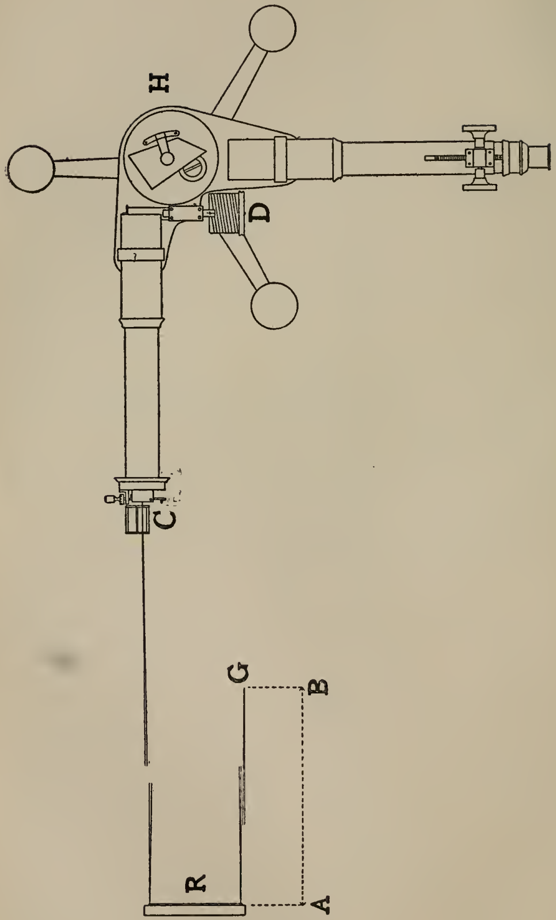

Fig. 2.

drum, D. In other words, all inconveniences attendant either upon the calibration of the spectroscope or upon subsequent references to a calibration curve, were avoided by the construction of the apparatus itself.

Secondly, all horizontal plane sections of the single glass prism were equal trapeziums; consequently, the beam of light, after entering the prism at the face nearest to the collimator, experienced one total interior reflection before it suffered final refraction out into the air opposite the telescope objective. This reflection diminished greatly the curvature in the field of view of all spectral lines of which the light had not passed through the prism, at the angle of minimum deviation. Therefore, it was possible to use a greater length of slit and wider field of view than would have been justifiable with the usual type of triangular prism of equal dispersion. The chief practical advantage of the wide field of view was that two different spectra could be seen in this field, the one above the other, and readings could be taken directly from the graduated drum D, without any appreciable danger arising from curvature of spectral images.

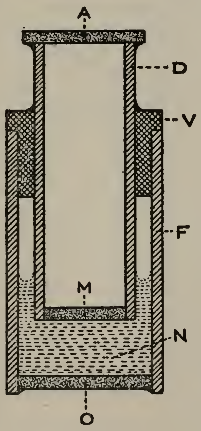

Fig. 3.

The Cells.—For photographic purposes two cells were used in the study of aqueous solutions. One of these is shown in vertical section in Fig. 3. The diagram is of natural size. The cell was designed to fulfil 5 conditions; (i) to transmit, without sensible selective absorption, all radiations between wave lengths 0.80 μ and 0.20 μ; (ii) not to be acted upon chemically by the solutions placed in the cell; (iii) to cause the incident and emergent surfaces of the absorbing liquid to be plane and practically parallel; (iv) to be capable of adjustment with respect to the length of the column of liquid traversed by the light, and (v) to keep itself as clean as possible when in the immediate vicinity of the spark. The parts of the cell may be briefly described as follows. D and F were short sections of glass tubing, the ends of which were ground at right angles to their respective axes of revolution. A plane parallel plate of quartz M, was cemented in the lower end of tube D, and a similar quartz plate O, was cemented to the inside of the tube F, near the lower end of this tube. The position of the latter quartz plate relative to the end of the larger glass tube made it possible to slide the cell around on its lower end as much as desired, without scratching the under polished surface of the quartz, and without causing dust particles to adhere to it. It was necessary, of course, to use quartz in order to transmit the shorter ultra-violet waves. V shows a hard rubber cylinder, carefully turned in a lathe to fit neatly the outside of tube D. The collar or flange of this cylinder, when the cell was in adjustment, rested on the top of a larger glass tube in such a position as to establish parallelism between the quartz plates M and O. The smaller glass tube and the vulcanized ring were prevented from sliding along each other by a small amount of cement. It was very easy to scrape off this cement and to replace it subsequently, whenever it became necessary or desirable to alter the depth of the column of liquid between the lower quartz plates. The quartz plate A was an essential part of the cell. When it was not present, the passing of the spark between the electrodes above the cell produced violent disturbance in the column of air in the tube D, which resulted in the deposition on the quartz plate M of the decomposition deposits of the electrode, *i. e.*, the oxides of cadmium, zinc, etc. Such a coating of foreign matter on the quartz, of course, could not be permitted. Care had to be taken to imprison dry air in the tube D when the plate A was cemented to the glass, because when this precaution was omitted a thin layer of moisture was deposited on the inner or opposing surfaces of the two quartz plates A and M, and produced spurious absorption effects on the spectrogram. After three of four photographic exposures with the spark had been made, the plate A invariably showed a thin whitish coating of the material, having boundaries which suggested a projection of the electrode on the quartz surface. This film was insoluble in water, and adhered very tenaciously to the polished quartz. It was easily removed, however, by rubbing with a piece of linen saturated with dilute hydrochloric acid. The coating was probably a mixture of the oxides of cadmium and zinc, driven hard against the quartz by the explosive violence of the spark. N shows the absorbing liquid in the cell. The light passed first through the quartz plate A, then through the dry air between A and M, then through the quartz plate M, next through the solution N, and finally through the quartz plate O. When the cell was filled with distilled water and extended as far as possible, no absorption, whether selective or general, could be detected photographically. Therefore, the selective absorption exhibited by the spectrograms was produced by the substance or substances in solution.

The cell just described was very well adapted to the study of plane parallel layers of liquid, having depths equal to and greater than 0.5 mm. On the contrary, its form did not lend itself as readily to the photographic study of extremely thin layers of very opaque solutions, as did that of another cell which had been designed by one of us[1] for an earlier investigation. A description of the cell last named may not be superfluous in this place. This piece of apparatus was used in the present work in such a manner as to impart to the absorbing liquid the form of a wedge or prism of zero thickness at the refracting edge. Consequently, the spectrograms obtained by this cell in the path of the beam of light, exhibit, graphically, the variation which the limits of the regions of selective absorption experience when the depth of absorbing liquid varies linearly and continuously from zero to a few tenths of a millimeter at the greatest thickness.

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[1] Uhler and Wood: *Loc. cit.*

The cell was made of 5 separable parts, as follows: (i) A brass framework upon which the other parts rested; (ii) a transparent tray without a lid, which confined the liquid in proper bounds; (iii) a transparent box-like system which gave the upper surface of the liquid the desired position; (iv) a vulcanized framework to hold the last-mentioned box in place; and (v) four mahogany pins or pegs to fasten the box to its framework.

(1) A side view of this work is presented in Fig. IV. This projection on a vertical plane is of natural size. There were 3 micrometer screws all of the same pitch, *viz.*, 1 turn = 1/48 in. = 0.053 cm. The heads of the screws are graduated on their upper surfaces in 10 equal parts. The screw T was in the immediate plane of the cell, while the remaining screws (T′ only is shown) were at the other end of the system, were equidistant from this plane, and as far apart as possible. The handle is denoted by HH. A black fiducial mark F, on a white ground, enabled the experimenter to tell what position the cell occupied with reference to the length of the slit of the spectrograph. The lower end of F moved over a scale parallel to the slit, and in the plane of the jaws of the latter.

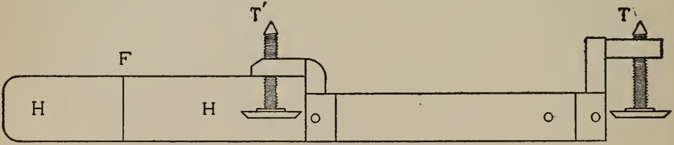

Fig. 4.

The flange at the bottom of the framework was made of brass, only 0.014 cm. thick, so that the absorbing liquid might be as near the slit as possible.

(2) An accurately ground, plane parallel plate of quartz, 40 mm. long, 18.5 mm. wide and 2 mm. thick, had cemented

to the perifery 4 rectangular sheets of glass, 8 mm. high. Hence the greatest depth of liquid which could be studied by the aid of this cell was 6 mm.

(3) In Fig. 5, *a*, *b*, *c* and *d* designate the vertices of a section of the quartz plate, made by a plane perpendicular to the plane whose trace is the line *ad*. A*b* was 2 mm., *ad* was 34.8 mm., and the angle between the planes of *ad* and *bc* was 55 minutes of arc. The horizontal width of the wedge was 10 mm. Glass walls surrounded three sides of the wedge as the outline indicates. The reason for using the wedge was to counteract the deviation and dispersion produced by the solution in the cell. The angle of the liquid wedge could be varied until the deviation affected by the quartz wedge nullified the average action of the absorbing solution. At first it was supposed that with liquid wedges of 15 or 20 minutes of arc, a plane parallel quartz plate could be used successfully instead of the quartz wedge. Actual tests, however, showed that a plane parallel plate could not be relied upon, in general, to give correct results. Finally, the quartz wedge was made with the utmost care by an expert optician, special pains being taken to have the edge through D perpendicular to the plane, *a*, *b*, *c*, *d*, as sharply defined as possible, and the surface whose traces are noted by *ad* and *bc* were accurately plane.

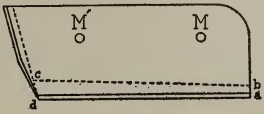

Fig. 5.

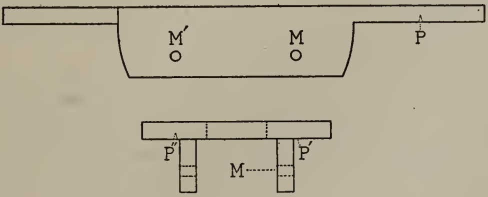

Fig. 6.

Fig. 6 represents a side view and an end view of the vulcanite frame, into which the box just described fitted. This frame was shaped out of a single block of vulcanite, since experience showed that a cemented system of several pieces was not desirable; also a dielectric was needed to keep the sparks from jumping to the screws. P indicates a little depression which fitted over the point of the screw T. P′ designates the end of a straight line along which the rounded extremity of the screw T′ slid. P″ is the cross-section of a shallow, V-shaped groove along which the pointed end of the third screw T″ likewise slid. The perforations MM′, etc., correspond to each other, and to the associated wooden pegs mentioned above as (5).

Fig. 7 is an unconventional sketch of the cell when completely assembled.

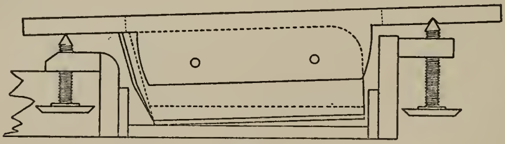

Fig. 7.

A cell of the construction just described is very well suited to the study of thin layers of solutions, in solvents of relatively high boiling points, such as water and amyl alcohol, but unless inclosed in some suitable vessel it is not applicable to solvents of lower boiling points, such as methyl alcohol, ether, chloroform, acetone, etc.

The cell used for making eye observations with the spectroscope, had to be constructed in such a way as to enable the observer to see simultaneously in the field of view of the telescope the absorption spectra of two solutions. This was necessitated by the very indefinite limits of absorption possessed by most of the regions and bands of absorption of the substances studied, *i. e.*, salts of cobalt and copper. In other words, it would have meant little or nothing to have attempted to observe one solution at a time, by setting the vertical cross-hairs at some definite wave length and to have given the numerical value of this wave length as the limit of absorption or of transmission, since the gradation from complete transmission to total extinction was, in general, so very gradual as to make the setting just proposed practically impossible. Even if the cross-hairs had been set on a wave length for which it was estimated that the absorption was some definite fraction of complete extinction, this very act of estimation would have varied so greatly from one solution to the next as to cause the results to be imcomparable, and, hence, nearly worthless.

When, on the contrary, two absorption spectra are symmetrically placed in the field of view, it is easy to see at a glance all the qualitative differences between the two spectra, and, in addition, in many cases, to assign a number of the right order of magnitude to the relative displacements of the regions of absorption and of transmission in the superincumbent spectral bands.

Obviously, the light incident upon one of the solutions had to be of equal intensity to the light of the same wave length incident upon the other solution. Two modes of procedure at least could lead to this result. One scheme would be to use two equal, but entirely independent cells, place them symmetrically with respect to the source of light and the slit of the collimator, and to send two beams of light one through each cell, over equal optical paths (except the absorbing liquids) by means of two trains of reflectors or lenses suitably placed and adjusted. This plan was given a very thorough test, and was finally abandoned for the one explained below. for the reason that by the above-mentioned scheme it was necessarily troublesome to maintain two independent trains of reflectors or lenses, or totally reflecting prisms, which would produce in the field of view when the cells were removed, two emission spectra of exactly equal intensity and also close together.

A much simpler arrangement, and one which left nothing of a practical nature to be desired, was the following (*vide* Fig. 2): Light emitted by the Nernst glower G, fell upon the concave speculum reflector R. This reflector was the unruled plate for a concave grating. The reflected beam came to a focus at the slit of the collimator, *i. e.*, the axis of the image of the glower coincided with that of the slit. Since the distance between *a* and *b* was 286.5 cm. and the distance between the reflector and the slit was 305 cm. (10 ft.) the beam of light did not greatly exceed the width of the glower's image for a distance of 3 or 4 cm. on both sides of the precise image. Consequently, when a cell of length less than 3 cm. and so constructed as to contain two solutions separated by a very thin diaphragm, was placed in contact with the slit jaws, any differences in the spectra of the light transmitted by the two liquids were correctly ascribed either to differences in absorption, or to inequalities in the transparency of the ends of the compartments of the compound cell. It was possible, of course, to make the halves of the cell so nearly alike as to produce no differential influence on the transmitted beams which could be detected visually. Even if this effective equality in the compartments of the cell could not have been realized, it would have been a comparatively simple matter to have interchanged the solutions in these compartments, and to have observed the phenomena which remained constant, and which were, therefore, due to the absorption of the liquids and not to the containing walls.

The more exact details and dimensions of the cell will now be given. The lower compartment was a box made of 5 rectangular strips of glass, cemented together. Its interior dimensions were, length 2.5 cm., width 2 cm. and depth 1 cm. The upper compartment was made of 4 vertical glass walls cemented together at the edges, and to a sheet of platinum foil as a bottom. The interior of this little box was, length 2.5 cm., width 0.94 cm. and depth 1 cm. The platinum foil was 0.06 mm. thick. Care was taken to make the 4 end pieces of glass of the same thickness, and from the same sheet. These ends were parallel to each other, and at right angles both to the bottoms and to the side walls of the respective compartments. Platinum was used as the partition between the boxes because it is opaque to visible radiations, and because it is not acted upon chemically by the solutions which came in contact with it. The foil was selected as thin as was consistent with rigidity, so as to produce as narrow a band of separation between the two transmitted portions of the main incident beam as possible. With this same object in view, the least bit of cement was used to make the lower surfaces of the glass ends of the upper compartment adhere to the platinum. The two boxes were made separate and distinct, so as to facilitate washing, drying, etc. The lower compartment was made wider than the upper, so that when the latter was resting in position on top of the former, it was a simple matter to pour a given solution into the lower compartment until it came in contact with, and wetted the entire under surface of the platinum. Consequently, the liquids were as close together as the thickness of the platinum (0.061 mm.), and their spectra appeared sufficiently near in the field of view of the telescope to admit of accurate and easy comparisons.

A suitable stand for this apparatus was fitted with leveling screws, which enabled the experimenter to adjust the cell so that the plane of the platinum partition contained the axis of the incident beam, at the same time that the ends of the cell were perpendicular to this line.

Freezing Point Apparatus.—This system was of the improved Beckmann type, which can be found described in so many places that mere reference to it is quite sufficient here. The thermometer used with this apparatus was also of the Beckmann type. The smallest spaces on the stem of the thermometer signified 0°.02, and the total range of scale was 12°.

For temperatures lower than 10° or 11° below zero, 2 alcohol thermometers were employed. These instruments are graduated in 0°.5, and the lowest temperatures which they could register were, respectively, 55° and 82°.5 below the standard freezing-point of water.

With the Beckmann apparatus a mixture of ice, water and sodium chloride was used as the refrigerating agent. With the alcohol thermometers a suitable mixture of solid carbon dioxide and ethyl alcohol was employed.

Conductivity Apparatus.—The usual combination of a Wheatstone slide-bridge, with a small induction coil and telephone receiver, was used. The conductivity cell was of the U-tube pattern,[1] since most of the solutions were too concentrated to give sharp tone minima in cells of less ohmic resistance. All of the measurements for this system were made at 0°. Every necessary precaution was taken to obtain reliable data.

THE MAKING OF THE PHOTOGRAPHS.

Photographic Material.—Because of the short radius of curvature of the focal surface (about 49 cm.), celluloid films were employed in the majority of cases. The films used throughout were M. A. Seed's "L-ortho," cut, negative films, size 5 inches by 7 inches. The emulsion is by no means equally sensitive over the field of wave lengths studied photographically, *i. e.*, from 0.20 μ to 0.63 μ. The chief maximum of sensitiveness is in the yellow, at about 0.56 μ. A weaker maximum is near 0.49 μ. The middle of the less sensitive intervening region was very roughly 0.52 μ. For the short exposures given throughout, these films are not appreciably influenced by wave lengths longer than about 0.61 μ. Consequently, the dark regions extending from about 0.61 μ to the longer wave length end of such spectrograms as were obtained by the use of the Seed films, do not denote absence of light due to the absorption of some given solution, but they make manifest the lack of sensitiveness of the emulsion to the portion of the spectrum under consideration. The resultant effect of the Nernst glower and the Seed emulsion is best understood by referring to Plate I(*a*) for which the times for exposure were, in order, 2 seconds, 5 seconds, 15 seconds, 30 seconds, 1 minute, 2 minutes and 3 minutes. Various schemes to make the resultant action from the light of the Nernst glower and the Seed emulsion more uniform were tried, and other makes of films were tested, but no improvement on the simple combination of the source of light and emulsion just named was found. In fact, other photographic films did not act as well, on the whole, as those furnished by the Seed

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[1] Jones and Getman: Z. phys. Chem., 49, 389 (1904).

Company. The films used were good in the ultra-violet, as is shown by the fact that with an exposure of 5 minutes the aluminium line at about 0.185 μ was clearly recorded, notwithstanding that the grating of the spectrograph was employed to disperse the light. When inspecting the photographs of absorption spectra, care must be taken to distinguish between possible spurious effects, arising from the maxima and minima of sensitiveness of the Seed films, on the one hand, and the phenomena of true absorption on the other. Observe the apparent band in the green as shown by Plate I(*a*).

As a check on the results obtained with the films, as well as to fill in the gap between about 0.59 μ and the nearer end of the field of view of the spectrograph, Cramer "Trichromatic" plates were used, since they were found to be the most satisfactory. The plates being plane and too rigid to be curved around into the focal surface of the grating had to occupy a mean position with respect to this surface. Since only a comparatively small region of wave lengths was recorded on the plates, no measurable errors were introduced. In fact, in the region considered, the second order ultra-violet of a discontinuous spectrum taken on a film and on a plate could be superposed line for line.

Sources of Light.—The sources of light and the selection of photographic material best suited for spectrographic work had previously been investigated by one[1] of us in an earlier research.

Nevertheless, a few words relative to these points may not be superfluous in this place.

For wave lengths from "above" 0.65 μ to "below" 0.326 μ, and for exposures of 2 minutes or less, the Nernst glower was found to be the most satisfactory. Prevailing circumstances made desirable the use of 106 volt glowers on a circuit carrying about 133 cycles. The emissivity of the Nernst lamp varies so very greatly with the electromotive force impressed upon its terminals, that it was obligatory to keep in series with the glower a Thomson A. C. ammeter, having a range from 0 to 2 amperes, and graduated directly to 0.02 ampere. Fluctuations of more than 0.02 ampere invariably resulted in a spoiled photograph. Therefore, boxes containing variable metallic resistance were maintained in series with the ammeter, and thus, in spite of large changes of the load on the dynamo, due to other circuits, it was possible to prevent the effective current in the filament from changing by more than 0.01 ampere. The current was always 0.8 of an ampere. The ammeter was appreciably more sensitive to small changes in the terminal voltage than a comparably graduated Thomson A. C. voltmeter, because the current shunted through the voltmeter was not negligible in comparison with the current which fed the glower. Among other sources, the electric arc was given a fair trial and discarded, for two reasons. First, because of the intensity of the carbon and cyanogen bands; and second, because of the inconveniences resulting from its unsteadiness and great emission of heat.

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[1] Uhler and Wood: *Loc. cit.*

For wave lengths between the strong ultra-violet of the Nernst glower and 0.20 μ a spark discharge in air of about 1 cm. in length was used. One electrode was composed of an alloy of equal parts by weight of cadmium and zinc, and the other was made of sheet brass. The alloy wore away so rapidly that the brass electrode was employed to diminish the mechanical labor attendant upon sparking the terminals. In order to produce a source of ultra-violet light which would have the same intensity from one end of the slit of the spectrograph to the other, for any one wave length, the electrodes were made in the shape of wedges or chisels, with the sharp edges parallel to the slit. The well-known distribution of a rapidly alternating current, necessitated curving the edges of the electrodes so that they were somewhat closer together at the middle than at the ends. Due to the tearing away of the metal and to various other causes, the innumerable thread-like sparks change the position of their ends so rapidly, that the integrating action of the photographic film recorded a perfectly uniform negative for exposure of 15 seconds or more. The electrodes had to be kept sharp and smooth, since when this was neglected, the elementary sparks persisted much longer in one position than in another and, consequently, caused streaks of varying intensity to run along the negatives parallel to their length.

The current for the spark was obtained in the following manner: An alternating electromotive force of about 106 volts (133 cycles) was impressed on the terminals of an induction coil of unknown ratio of turns. Eight or nine amperes commonly flowed in the primary. The interrupter of the coil was thrown out of circuit, and the coil therefore performed the functions of a transformer. In parallel with the secondary was placed a Leyden jar about 18 inches high, and of unmeasured capacity. No auxiliary spark was introduced.

Exposures and Spectrograms.—When the complete spectrograms of a series of solutions were to be obtained, the succession of operations was, in general, as follows:

First, the depth of the cell for plane parallel layers of solution was made such that, judging from experience, and being guided by the depth of the color of the extreme solutions in their bottles, it would be neither too shallow to give appreciable absorption when the cell contained the most dilute solution, nor too deep to transmit enough light to affect the photographic plate when the liquid of deepest color was placed in the cell.

Second, a portion of each of the extreme solutions was successively poured into the cell which was, of course, clean and dry, and the corresponding spectrum observed by the aid of the spectrograph and a suitable eye-piece. In all cases, except those for which the solutions of deepest color were practically opaque to light for all depths greater than 0.5 mm., a depth of cell was soon found which enabled the absorption spectra of all the solutions of the series to be photographed on the same film, and with exposures of equal duration.

When 15 or 16 solutions belonged to one series, and this was often the case, the first 8 solutions were photographed on one-half of a complete 5 inches by 7 inches negative film, and then the remaining solutions had their absorption spectra photographically recorded on the other half of the same film. This break in the continuity of the work was due to the fact that the capacity of the camera was limited to 8 spectral bands, each 6 mm. wide and spaced 0.05 mm. apart.

Except when there was some very good reasons for doing otherwise, care was taken to develop the halves of a film simultaneously, so as to subject all of the exposures to exactly the same chemical conditions. When the series of solutions comprised less than 15 members but more than 8, then the change from one-half of the film to the other was generally made as soon as the number of solutions which had already been photographed either equaled the number of those which remained or exceeded the latter number by unity. The reason for so doing is, doubtless, obvious. For any one solution the exposure with the Nernst glower was made first, the screen Q of the spectrograph being, of course, vertical. Then this screen was set horizontal, and the spark run for a definite length of time. Usually the light from the glower was caused to pass through the absorbing liquid for 1.5 minutes, while that from the spark for $1^1/_3$ minutes. These two intervals of time were so related that when no medium exhibiting appreciable absorption was in the path of the beams of light, the photographic impressions successively produced by the radiations from the Nernst glower and by the spark, blended into each other so well, that no discontinuity in the continuous background could be detected. The lengths of time of the exposures will be given only when they differ from 90 seconds and 80 seconds, respectively, for the glower and spark. The screen Q performed the function of protecting the negative film from contamination from the spectrum of the second order, which otherwise would have been superposed upon the spectrum of the first order.

As soon as the light transmitted by one solution had been recorded photographically, another solution was substituted for the preceding one, and also the film holder was moved along by the rack and pinion system through about 6.5 mm.; that is, until a strip of unexposed film came into the field of view of the grating. This strip was at a distance of a 0.5 mm. or so from the region previously exposed. After all of the 8 or less complete photographic strips on one-half film had been exposed, the proper opening in the slide screen or shutter L [*vide* Fig. 1], was brought into position and the comparison spectrum impressed.

When spectrograms were made with trichromatic plates and the cell under consideration, the sequence of events was essentially the same as that just explained, except in so far as the exposure of the solutions to the light from the spark were omitted. Further, since plates of this kind are not as sensitive to orange and red light, as the Seed films are to most of the more refrangible colors, the time of exposure to the glower's radiations was usually 2 minutes.

Since the complete description of the manner of experimenting with the wedge-shaped cell has already been given elsewhere, and especially because a relatively small number of spectrograms were made with this cell in the present investigation, it seems desirable to discuss this matter only briefly here.

The length of the liquid wedge at right angles to its reflecting edge being about 3.5 cm. and the length of the spectrograph's slit being a little over 1 cm., the chief operation in manipulation of the wedge cell consisted in moving it over the slit jaws and parallel to the slit by proper amounts between successive exposures. Experience showed that the correct distance to move the cell was exactly 10.5 mm. The film holder had, of course, to be moved through corresponding distances between the respective exposures just mentioned. Consequently, the resulting spectrograms consist of 3 photographic impressions placed side by side and close together.

The edge of a spectrogram nearest to the comparison spectrum was produced by light which had passed through the thinnest layer of absorbing liquid, usually of zero depth; while the most remote edge resulted from the radiations transmitted by the deepest layer of solution. The slit width of the spectrograph was generally 0.08 mm.

Plates.—Before entering upon the presentation and discussion of the experimental results, a few words must be devoted to certain details which are common to most or all of the plates showing the absorption spectra of the solutions studied.

In the first place, when more than 8 strips belong to a plate, the corresponding photographic positives had to be made by placing the 2 half-negatives in the printing frame, with their edges as close together as possible, and with the line of the same wave length exactly opposite to one another, *i. e.*, in proper register. In general, the line of contact of the 2 half-films shows in the figures as a streak of intensity different from that of the adjacent portions of the print, and extending from one end of the figure to the other. It is more than likely that slight errors in wave length have been introduced in some cases by this process of reproduction, which, however, was necessitated by the limited capacity of the film holder. In most cases these errors can be fully allowed for, by observing the relative displacement of the two segments of some chosen sharp emission line, which appear on the two photographic strips lying on both sides of, and closest to the above-mentioned streak. Whenever this line of demarkation does not show distinctly on the figure, a definite statement will be made in the text as to where the change from one half-film to the other is. However, in cases when no emission lines are present on the two strips bordering on the streak, the reader has no very good means of telling whether the half-films were in exact register or not, and, therefore, he will have to assume that no appreciable error has been introduced in this manner. Moreover, shifts in wave lengths due to the motion of the film holder and its guides or ways, are present in most of the figures. These displacements can be measured and allowed for in the manner suggested above. It must be borne in mind that the solutions studied, present such washed out limits to most of their regions of absorption, that it is not possible to assign numbers to the wave lengths of these boundaries, which would be nearly as accurate as the determination of the relative shifts of the parallel photographic strips. Moreover, with bands of absorption of the type just referred to, their apparent ends would be displaced in wave length by various experimental causes, such as variations in the intensity of incident light, changes in the time of exposure to the radiations, changes in the duration of development, variations in the temperature and composition of the developer, etc. The best that could be hoped for was to obtain parallel spectrographic strips of the solutions of a given series, which exhibit the spectral changes caused by the solutions themselves, and only by the solutions, extreme care being taken to keep all other conditions as nearly constant as possible. The figures, therefore, show the relative changes in the absorption spectra of the solutions of one set with accuracy. Whenever there was the slightest possibility of spurious results arising from the chief maxima and minima of sensibility of the Seed emulsion, the results were checked by taking additional plates with the Cramer trichromatic emulsion, which has not the same sensibility curve as the Seed film. In all cases the series of eye observations with the spectroscope, not only supplement the photographic data in the red, but they also serve as an additional qualitative check on the entire visible region.

For comparatively accurate estimations of wave lengths, one comparison spectrum of the emission lines of the spark has been reproduced in each photographic figure. The most intense and sharpest lines have been numbered in Plate I(*a*). This plate serves as a key to the table of wave lengths given in a later paragraph.[1]

Since the spark lines of cadmium, zinc, oxygen and nitrogen are not equally spaced, the comparison spectrum mentioned above, together with its key and table, is very inconvenient for most purposes of reference. Consequently, a numbered linear scale of wave lengths has been printed by the side of each complete spectrogram. Although it is not professed that these scales are as accurate as they are suggestive and convenient, nevertheless, it is only fair to call attention briefly to the chief errors possessed by them. As is well-known, a concave grating gives spectra which depart more and more from normality, as we recede from the principal axis of the reflector on which the lines of the grating are ruled. Therefore, a strictly linear scale cannot correctly register all the wave lengths of a grating spectrum. Nevertheless, the grating belonging to the spectrograph was of such short focus that for the region of wave lengths of the first order spectrum used, the error just mentioned was negligible in comparison with those explained below.

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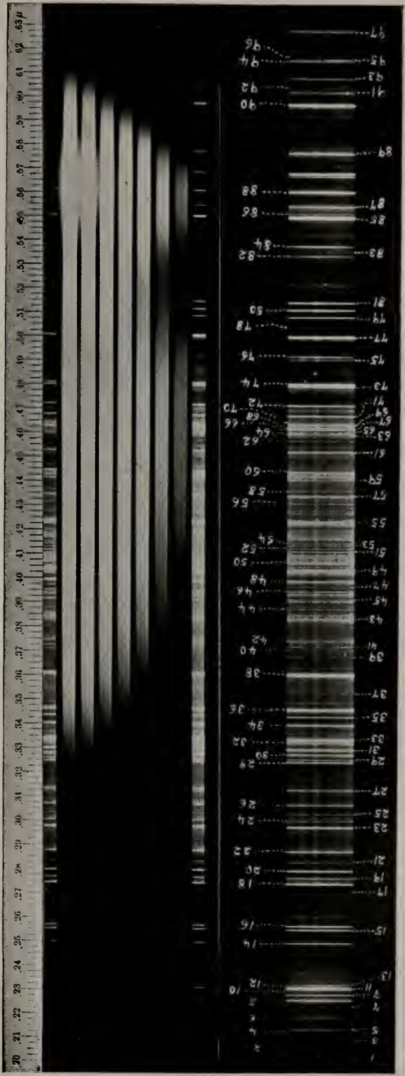
[1] Uhler and Wood: *Loc. cit.*

It is a well-known fact that celluloid negative films, after development, fixing and drying, differ appreciably in length from the same linear dimension which they possessed before being so treated. If all the films of one make would behave quantitatively in exactly the same way, the variations in length to which attention has just been called, would be of no importance from the present point of view. But films of the same kind change by very different amounts, and this phenomenon is inconvenient, to say the least. Therefore, to have linear scales to fit accurately each and every one of the complete spectrograms, it would be necessary to make as many different scales as there are different distances between the extreme spectral lines, say, throughout the entire series of spectrograms. Obviously, to do this would entail an amount of labor which would be utterly disproportionate to the gain in accuracy finally obtained. Consequently, only 4 or 5 negative scales of different total length were obtained by photographic production from the same paper scale, which was ruled and numbered for the present work. Since the negative scales cover the entire range of variation in length of the spectrograms, the wave lengths of selected lines, when read off from the scales on the published plates, ought not to contain any large error.

In making the positives the scale line numbered 48 was placed opposite to the corresponding strong emission line of the comparison spectrum. The latter line has a wave length of about 4800.1 Ångström units, and is designated by 73 on Plate I(*b*). It is probable that in a few cases the two lines just named, the one on the negative scale and the other on the negative spectrogram, were displaced a little with respect to each other in the process of printing.

To avoid having the lines of the numbered scale too close together, each of the smallest intervals denotes 25 Ångström units.



Plates I(a) and I(b).

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The wave lengths of the numbered lines of Plate I(*b*)[1] were derived from the two following sources:

"An Introduction to the Study of Spectrum Analysis," by W. M. Watts.

"Measurements of the Wave Lengths of Lines of High Refrangibility in the Spectra of Elementary Substances," Hartly and Adeney. From the *Philosophical Transactions* of the Royal Society, Part I, 1884.

1.	2024.2	Zn.
2.	2060.8	Zn.
	2062.8	Zn.
3.	2099.0	Zn.
4.	2138.3	Zn.
5.	2144.5	Cd.
6.	2194.7	Cd.
7.	2239.9	Cd.
8.	2265.1	Cd.
9.	2288.1	Cd.
10.	2306.7	Cd.
11.	2313.0	Cd.
12.	2321.2	Cd.
13.	2329.3	Cd.
14.	2502.1	Zn.
15.	2558.0	Zn.
16.	2573.1	Cd.
17.	2710.1	Air.
	2712.6	Zn.
18.	2748.7	Cd.
19.	2770.9	Zn.
20.	2801.0	Zn.
21.	2837.0	Cd.
22.	2880.9	Cd.
23.	2980.8	Cd.
24.	3007.0	Air.
25.	3035.9	Zn.
26.	3072.2	Zn.
	3076.0	Zn.
27.	3133.3	Cd.
28.	3250.5	Cd.
29.	3261.2	Cd.
30.	3282.4	Zn.
31.	3302.7	Zn.
32.	3329.3	Air.
	3331.5	Air.
33.	3345.1	Zn.
	3345.5	Zn.
34.	3403.7	Cd.
35.	3436.9	Air.
36.	3466.3	Cd.
	3467.8	Cd.
37.	3535.0	Cd.
38.	3610.7	Cd.
	3613.0	Cd.
39.	3682.6	?
40.	3712.2	Air.
41.	3726.6	Air.
42.	3749.8	Air.
43.	3839.3	Air.
	3841.7	Air.
44.	3881.9	Air.
45.	3919.2	Air.
46.	3954.8	Air.
	3956.2	Air.
47.	3972.5	Air.
48.	3995.1	Air.
49.	4041.4	Air.
50.	4070.0	Air.
	4072.4	Air.
	4076.1	Air.
51.	4119.4	Air.
52.	4132.8	Air.
	4133.8	Air.
53.	4145.9	Air.
54.	4151.9	Air.
	4153.6	Air.

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[1] The negative was not a single exposure. To stand reproduction the extreme ultra-violet was "favored."

55.	4228.5	Air.	
	4236.7	Air.	
	4241.9	Air.	
56.	4316.2	Air.	
	4318.7	Air.	
57.	4349.5	Air.	
58.	4367.9	Air.	
59.	4415.1	Air.	
60.	4447.1	Air.	
	4447.2	Air.	
61.	4530.1	Air.	
62.	4576.2	Cd.	9_2.[1]
63.	4601.6	Air.	
64.	4607.3	Air.	
65.	4614.0	Air.	
66.	4621.6	Air.	
67.	4626.0	Cd.	11_2.
68.	4630.7	Air.	
69.	4641.9	Air.	
	4643.4	Air.	
70.	4649.2	Air.	
71.	4680.4	Zn.	
72.	4722.3	Zn.	
73.	4800.1	Cd.	
74.	4810.7	Zn.	
75.	4912.3	Zn.	
76.	4924.8	Zn.	
77.	5002.7	Air.	
	5005.7	Air.	
78.	5045.7	Air.	
79.	5086.1	Cd.	
80.	5116.0	Zn.	15_2.
81.	5146.2	Cd.	16_2.
82.	5338.6	Cd.	
83.	5354.4	Cd.	—$_2$.
84.	5379.3	Cd.	
85.	5497.4	Cd.	18_2.
86.	5509.0	Zn.	—$_2$.
87.	5541.8	Zn.	19_2.
88.	5602.0	Zn.	20_2.
89.	5761.8	Cd.	22_2.
90.	5961.6	Cd.	23_2.
91.	6014.0	Air	24_2.
92.	6035.0	Zn.	—$_2$.
93.	6071.8	Zn.	25_2.
94.	6144.4	Zn.	26_2.
95.	6152.0	Zn.	26_2.
96.	6160.4	Cd.	—$_2$.
97.	6266.6	Cd.	27_2.

EXPERIMENTAL FACTS AND DATA.

In the succeeding pages the experimental material will be presented in the following order: All the facts obtained by spectrographic means, pertaining to the simple aqueous solutions containing cobalt chloride will be given first; then those relating to cupric chloride, and, finally, those pertaining to cupric bromide. Following this, the solutions obtained by adding calcium chloride, calcium bromide, or aluminium chloride, to the simple aqueous solutions, will be taken up in the order in which the dehydrating agents have been named. For any set of solutions, the data obtained by the photographic method will appear immediately after the record of the concentrations. The results of eye observations with the spectroscope will then be presented, and, following this, the freezing point lowering will be given. Conductivity data expressed in reciprocal ohms and reciprocal centimeters will then be presented and, finally, attention will be called to any other facts which have been noted.

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[1] Subscripts 2 denote the second order.

Solutions.—The aqueous solutions investigated are made up as follows: A chosen volume of the mother solution of a colored salt was measured out from a burette, into a measuring flask of known capacity. The portion of solution in the flask was then diluted by the addition of pure water which had been distilled several times, so that its conductivity was as low as 1.1×10^{-7} at 0° on the average, until the volume of the resulting homogeneous liquid was exactly equal to the fixed capacity of the flask. The same flask was used in making up all the solutions studied throughout the entire investigation. The concentrations will always be expressed as multiples of normal. The term "normal" will be used exclusively to mean gram-molecular normal; *i. e.*, a liter of solution which contains just as many grams of anhydrous salt as there are units in the number expressing the molecular weight of the salt, is defined as "normal." Hence, if a liquid is composed of n gram-molecules of salt in a liter of solution, its concentration is n times normal; n can have any positive value, integral or fractional. In general, several solutions of one set were made up with reference to their colors; in other words, in such a manner as to employ as wide a range of concentrations as could be conveniently photographed, and at the same time to bring out the delicate changes in tint by having the successive differences in concentration as small as desirable.

When a solution contained both a colored salt and a colorless dehydrating agent, it was prepared as follows: A certain known volume of the mother solution of the colored salt was measured out into the flask mentioned above. Then a definite volume of the mother solution of the dehydrating agent was poured into the flask containing the colored liquid. The sum of the 2 volumes just specified was less than the fixed capacity of the flask. In special cases shrinkage in volume on mixing would make this statement slightly inexact. Finally, the mixture of the mother solutions was made up to the full volume of the measuring flask by the addition of pure water. In a series of solutions containing the same pair of salts two things were kept constant. First, the mass of colored salt present, and second, the total volume of the solution. The chief variable was the mass of dehydrating agent in the several solutions. As formerly, the color changes were the criteria governing the number and respective concentrations of the solutions of any one series. It was not deemed necessary to determine the specific gravities of the liquids studied. The details relating to the individual salts will now be considered.

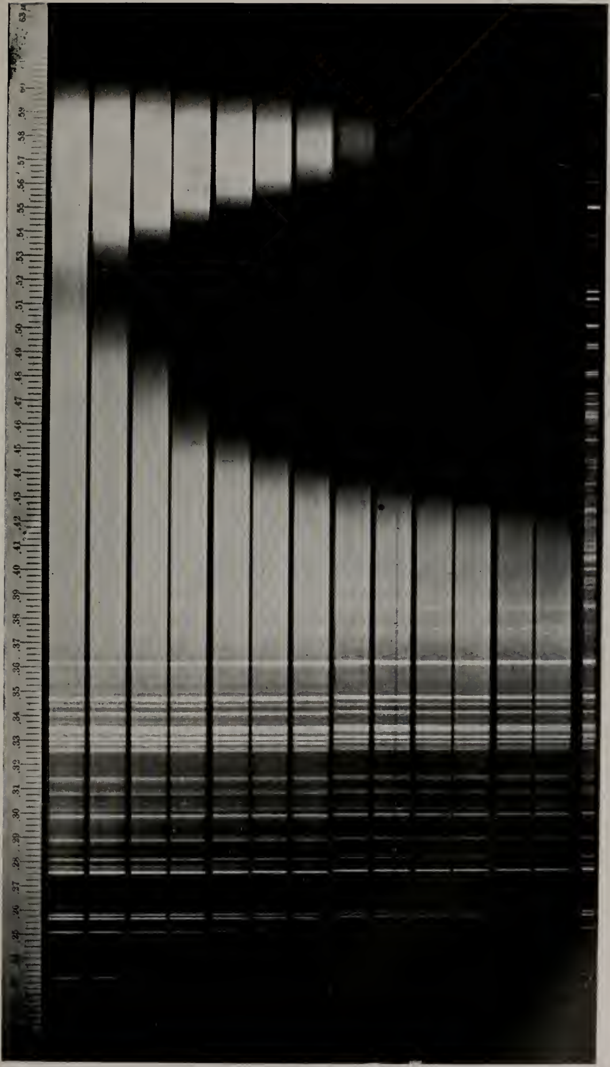
Cobalt Chloride.—(See Plates II., III(*a*), which has been reduced to seven-eighths of its original size, and IV(*a*).) The concentrations of the solutions were 0.217, 0.379, 0.542, 0.759, 0.976, 1.192, 1.409, 1.626, 1.843, 2.060, 2.276, 2.493 and 2.710. Therefore, the first 2 increments of concentration were each equal to 0.1626 and each of the remaining successive differences equal to 0.2168.

The number 2.710 belongs to the mother solution of cobalt chloride. The color of the liquids increased in depth from a delicate pink or rose color to a very dark red. In layers of more than about 1 cc. in thickness, the more concentrated solutions were opaque to ordinary light. The solution whose concentration was 0.217 N, gave the absorption spectrum shown by the photographic strip nearest to the numbered scale of Plate II. The next strip corresponds to the concentration 0.379, etc., across the spectrogram. Thus, the strip nearest to the comparison spectrum is associated with the mother solution. The common depth of the absorbing layers of liquid was 0.67 cm. The spectrogram shows 2 regions of absorption, the one in the remote ultra-violet and the other in the blue and green.

The most dilute solution transmitted the line at 2138.3, but nothing of shorter wave length. All numerical data were derived from the negatives and not from the plates.

The background stops at about 2265. The most concentrated solution barely transmitted the line of wave length 2502.1, and cut out practically all the continuous background which is more refrangible than 2748, due regard being had for

Plate II.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the successive increments of concentration of the solution. For the most dilute solution, the maximum of absorption in the green was at about 0.515 μ. The general contour of the limits of ultra-violet transmission can best be understood by referring to Plate II.

The region of absorption encroached on the shorter wave lengths, more rapidly than on the longer ones. The asymmetry of the region may be due to the superposition of 2 close, unresolved bands, of which the more refrangible was the weaker. For the seventh solution of concentration 1.409, the middle of the photographic region for absorption was at 0.503 μ. The more refrangible end of this band was at about 0.432 μ for the more concentrated solution.

The absorption spectra of the 5 most concentrated solutions were photographed with a red sensitive plate, and the result is reproduced as Plate III(*a*). The depth of cell was 0.67 cm., as before, but the exposure with the Nernst filament was 2 minutes in length. The photographic limits of absorption of the solution of concentration 1.843 were about 0.438 μ and 0.565 μ, while those for the mother solution were about 0.427 μ and 0.585 μ. The apparent displacement of the middle of the band from 0.502 μ to 0.506 μ, with increasing concentration, is probably due, in part, to weak photographic action in the neighborhood of the less refrangible end of the absorption band of the most concentrated solution. Moreover, the negative plate was undeveloped.

Plate IV(*a*) shows the continuous variation of thickness of the absorption of the mother solution of cobalt chloride. The solution was placed in the wedge cell and consequently the depth varied linearly. To bring out the band in the blue-green, zero depth of absorbing layer could not be used. The least and greatest depths of liquid were 0.53 mm. and 1.09 mm., respectively, and the angle of the cell was 58′.5. As usual, the side of the spectrogram corresponding to the least depth of the liquid lies nearest to the comparison spectrum. The times of exposure for the glower and spark were 90 seconds and 80 seconds, respectively. The band in the blue-green has its centre about 0.520 μ. It seems to be slightly asymmetric, but this appearance is doubtless exaggerated by the great sensitiveness of the Seed film to yellow light. The end of the band in the extreme ultra-violet varies slightly with increasing thickness of the absorbing layer. Faint transmission begins about 0.245 μ. A negative taken with the cell set at an angle of 35′.1, and commencing at zero depth showed practically no band in the green, but it did show a definite curved line of absorption in the remote ultra-violet. A general idea of the course of this curve can probably be gathered from the following statements: The least trace of the zinc doublet at 2062 A. U. was shown at the very edge of the negative. The spectral lines of wave length 2144.5 and 2194.7 jutted out from the edge of the spectrogram, through distances of, approximately, 6 and 9 mm. The continuous background ended at 0.238 μ on the edge of the negative corresponding to the greatest depth of solution in the wedge.

Eye observations with the spectroscope showed the facts recorded below. The depth of the cell was the same as when photographic exposures were being made. For the solution of concentration 0.217, the spectrum began at about 0.775μ. No bands were visible in the red. The band in the blue-green was very faint and diffuse.

The solution of concentration 0.759 also showed no band in the red. The most intense absorption seemed to be at 0.525 μ, but the blue-violet side of the region was so much more diffuse than the yellow side, that not much importance should be attached to this number. Due allowance has been made for the fact that with a simple prism the dispersion increases as the wave length decreases. However, the spectroscopic observations confirm qualitatively the spectrographic results.

No bands could be seen in the red for the solution of concentration 1.409, and absorption was complete from about 0.558 μ to about 0.450 μ.

The violet was greatly dimmed.

Similarly, the solution of concentration 2.060 exhibited no bands in the red. The band in the midst of the visible region extended from 0.571 μ to, roughly, 0.488 μ. As previously, Plate III(a).

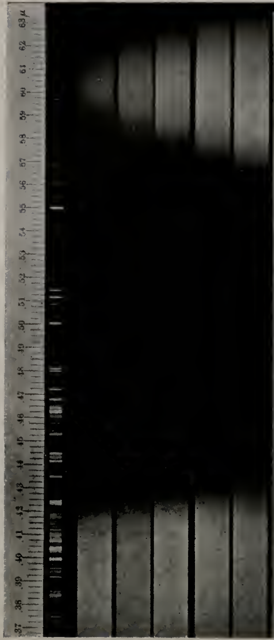
.37 .38 .39 .40 .41 .42 .43 .44 .45 .46 .47 .48 .49 .50 .51 .52 .53 .54 .55 .56 .57 .58 .59 .60 .61 .62 .63 μ

Plate III(b).

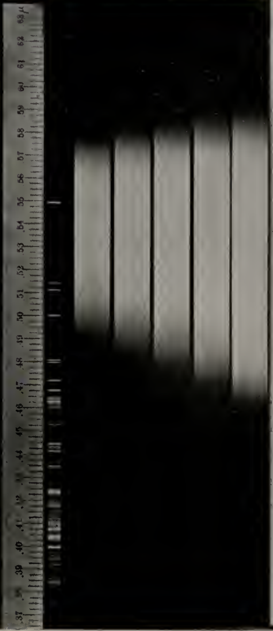
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Plate III(c).

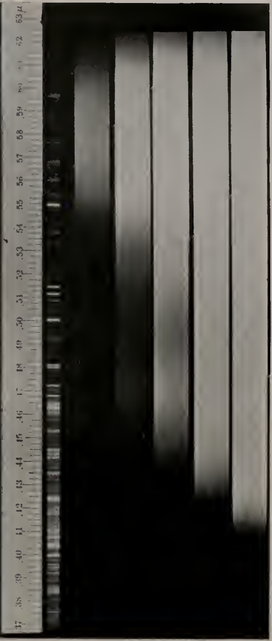
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Plate IV(a).

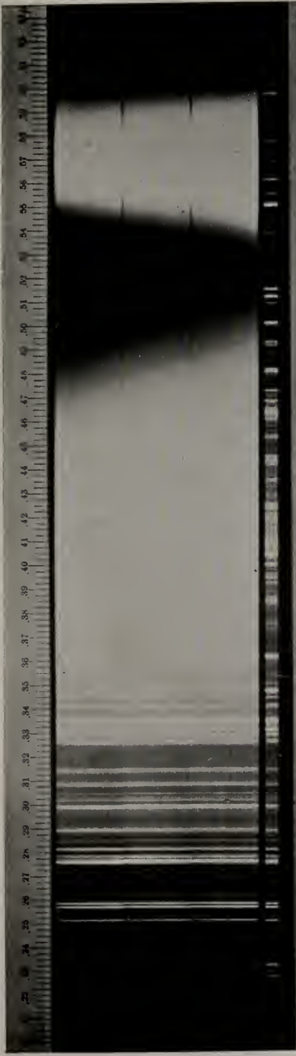
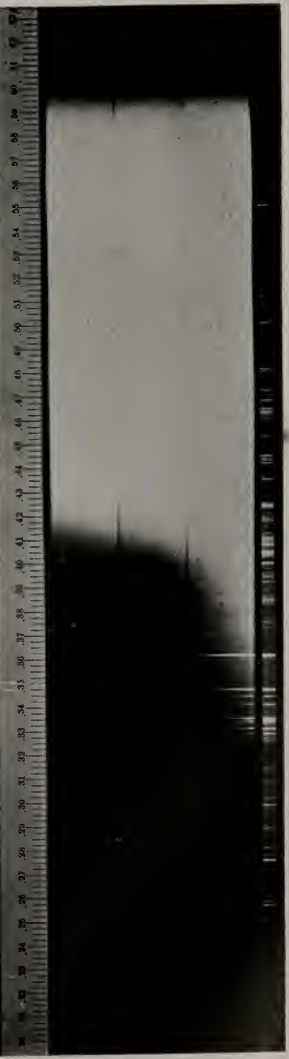


Plate IV(b).



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the end of the band nearer the yellow was much more definite than the end in the indigo. The violet was rather faintly transmitted.

The mother solution showed a series of weak bands in the red. Only the orange and certain parts of the red were transmitted, and the light was considerably weakened even in these regions. It would seem, at first sight, that the last statement is inconsistent with the wave length 0.432 μ, which the spectrogram gives as the extreme, least refrangible boundary of the region of transmission in the ultra-violet and violet, when the well-known fact that the average normal eye is sensitive to waves at least as short as 0.400 μ is taken into account. The apparent discrepancy is easily accounted for by the following considerations. The photographic film exerted an integrating action over a period of 90 seconds, whereas the retina does not add up successive stimuli of the same spot for nearly so long a time. Moreover, the dispersion of the spectroscope in the violet was much greater and the spectrum no brighter than that of the grating in the same region. The spectrum began about 0.773 μ. From this point the intensity of transmission rose gradually to a maximum, and then decreased to a faint minimum at 0.714 μ. This faint absorption band was followed by another one at 0.676 μ. The spot of maximum brightness between these bands was at about 0.669 μ. Between 0.67 μ and 0.59 μ the incident light had suffered less general absorption than anywhere else in the visible spectrum, with the exception that a faint, narrow absorption band was just noticeable at 0.636 μ. Transmission ceased at about 0.588 μ.

Cupric Chloride.—(See Plates III(*b*), IV(*b*), and V., which last has been reduced to three-fourths of its original size.) The concentrations of the solutions were 0.239, 0.318, 0.557, 0.795, 1.113, 1.272, 1.431, 1.590, 1.749, 2.067, 2.385, 2.073, 3.021, 3.339, 3.657 and 3.976. The successive differences in concentration were 0.079, 0.239, 0.239, 0.318, 0.159, 0.159. 0.159, 0.159, for the first 9 solutions, and 0.318 for all the rest. The last number belongs to the mother solution of copper chloride.

The color or the most dilute solution was a delicate blue, then, as the concentration increased, the color of the solutions passed through various shades of greenish blue or bluish green, of light green and, finally, the mother solution was a deep, dark green.

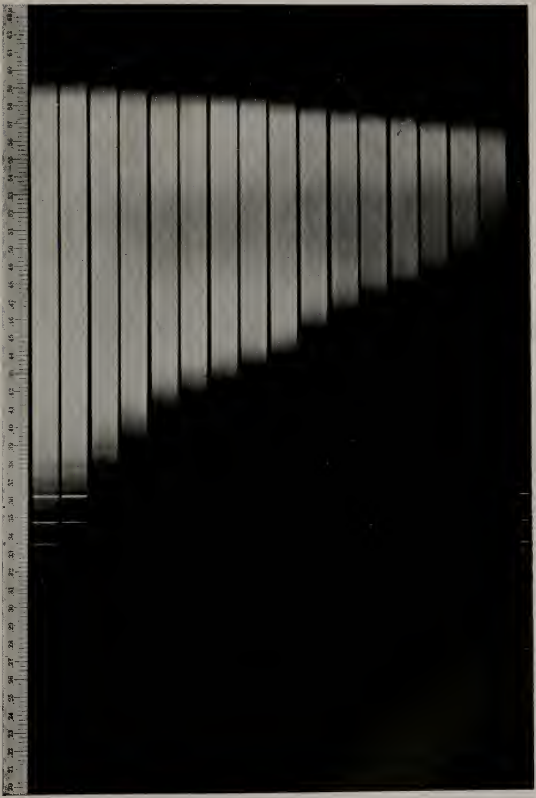
Plate V. will be considered first. The solution whose concentration was 0.239 N has its absorption spectrum shown by the photographic strip nearest to the numbered scale. The remaining strips succeed one another in the order of increasing concentration, so that the strip nearest to the comparison spectrum corresponds to the mother solution. The effective depth of the cell was 0.67 cm.

The spectrogram shows 2 regions of absorption, the one in the ultra-violet, violet-blue, etc., and the other in the orange. Absorption in the region last named is to be inferred from the fact that the ends of the photographic strips corresponding to the more concentrated solutions do not lie in a straight line at right angles to the length of the spectrogram, but they recede from the end of the plate as the concentrations increase.

If there has been no strong selective absorption in the yellow-orange, then all the photographic strips would have faded out at the same distance from the end of the plate, due simply to the lack of sensitivity of the Seed negative films to light of relatively small refrangibility. The most dilute solution transmitted a faint trace of the spark line at 3250.5, but nothing of shorter wave length. The absorption of solution of concentration 0.318 was very little more extended than that of the most dilute member of the series.

This is due to the fact that these 2 solutions did not differ greatly in concentration. To obtain the clearest view of the variation of absorption with concentration, it is best to fix the attention only upon those photographic strips that correspond to the solutions whose concentration differed by the same amount, *e. g.*, by 0.318. In other words, omit the first, second, third, sixth and eighth strips from consideration for a moment. It is then seen that a smooth curve is presented by the limits of the region which absorbs all of the shortest

Plate V.



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waves of light. Also the successive increments of absorption become less and less, as the concentrations of the solutions increase. For example, the seventh photographic strip ends about 200 A. U. farther along than the fifth strip. The twelfth, 90 units beyond the eleventh, and the sixteenth 55 units beyond the fifteenth. The region of transmission for the mother solution extended from about 0.483 μ to 0.574 μ.

The negative for Plate III(*b*) was obtained with a Cramer "Trichromatic" plate. The exposure for each of the 5 most concentrated solutions was 2 minutes in length. The depth of the cell was 0.67 cm., as before. This spectrogram shows correctly the limits of transmission not only at the blue side, but also towards the red, since the photographic plates would have been made deep black as far as its very ends, if the light had not passed through the absorbing layer of liquid. The limits of the region of transmission for the solution whose concentration was 2.073, were 0.460 μ and 0.593 μ, while the corresponding numbers for the mother solution were 0.485 μ and 0.583 μ. Therefore, the rate of increase for absorption is greater at the more refrangible end of this region than at the less refrangible end. In fact, the middle of the transparent region shifted towards the red by about 75 A. U. as the concentration increased from 2.073 to 3.976.

Plate IV(*b*) was obtained with the wedge-cell set at an angle of 19′.5 and starting with nearly zero depth. The thinnest layer transmitted a trace of the cadmium line at 3133.3. The boundary of the ultra-violet region of absorption then curved around as shown by Plate IV(*b*), and reached about 0.400 μ, corresponding to the thickest part of the wedge. The great intensity of the ultra-violet absorption is worthy of note.

Eye observations fully confirm the results obtained by the photographic method. For the most dilute solution, transmission began at about 0.727 μ, *i. e.*, in the bright red. As more and more concentrated solutions were observed, the absorption at the red end of the spectrum extended gradually to shorter and shorter wave lengths. The following numbers were recorded as the wave lengths of the extreme limits of visual transmission for the first, fourth, seventh, tenth, twelfth, fourteenth and sixteenth solutions, named in the order of increasing concentration, *viz.*, 0.727 μ, 0.677 μ, 0.646μ, 0.634 μ, 0.624 μ, 0.616 μ, and 0.660 μ, respectively. Reasons why the eye observations agree qualitatively, but not quantitatively, with the photographic results are too simple to need explanation. The limits of the more refrangible ends of the regions of transmission of the solutions, as obtained with the spectroscope, are not as satisfactory as the results obtained photographically, because the absorption fades away very gradually in the part of the spectrum under consideration. Therefore, no more wave lengths will be given for the simple solutions of copper chloride in water.

Cupric Bromide.—(See Plates III(*c*), VI. and VII(*b*).) The last two are reduced to three-fourths of the original size. The concentrations of the solutions photographed were 0.175, 0.350, 0.394, 0.437, 0.481, 0.525, 0.568, 0.612, 0.656, 0.700, 0.874, 1.049, 1.224, 1.399 and 1.574. The first, second, sixth and tenth solutions, as well as those having greater concentrations than the tenth, form a series in which the successive concentrations differ by the same amount, namely, by 0.175. The remaining solutions were interpolated in the series just mentioned, and the successive increments of concentration thus produced are all equal to 0.044, *i. e.*, to one-quarter of the greater common difference, 0.175. In this case the concentration of the mother solution was 2.186. The solutions, when in the plane parallel cell, which was adjusted at a depth of 2 mm., varied from almost no color for the most dilute solution, through different shades of clear green and yellowish-green, to a very dull brownish-green for the solution of concentration 1.574. In the bottles, of course, the colors were much deeper than in the cell, and the more concentrated solutions of the set photographed, together with the mother solution, were apparently opaque to light.

In Plate IV., as usual, the photographic strips showed the absorption spectra of the solutions of concentration 0.175 and 1.574 are adjacent, respectively, to the numbered scale and to the comparison spectrum. The 15 strips succeed one another in the order of increasing concentration. The most dilute solution transmitted an extremely faint trace of the line at 3250.5, but nothing of shorter wave length. Due regard being had for the successive difference in concentration, it is seen from the spectrogram that the region of absorption which includes the ultra-violet increases in a perfectly regular way for about the first 12 solutions. The thirteenth strip begins to show weak absorption at about 0.517 μ and the fourteenth brings out the presence of this band very noticeably. The long, prenumbra-like region, which extends from about 0.45 μ to 0.53 μ on the fourteenth strip, is entirely absent from the fifteenth. The shortest wave length recorded by the spectrogram for the most concentrated solution is, approximately, 0.543 μ. The last 3 or 4 photographic strips, which correspond to the more concentrated solutions, indicate the presence of a region of weak general absorption in the orange and red. In drawing conclusions from spectrograms of solutions of copper bromide, care must be taken to avoid errors which might arise from the maxima and minima of sensitivity of the photographic emulsions, especially when Seed orthochromatic films are involved [*vide* Plate I(*a*)].

The statements made above are substantiated for the 5 most concentrated solutions by Plate III(*c*), the negative for which was a "Trichromatic" Cramer plate. The cell was adjusted to a depth of 2 mm. as before, and the length of each exposure to the light from the Nernst glower was 2 minutes. That the absorption in the orange-red is weak, in general, is shown by the fact that 4 of the 5 photographic strips of the negatives were blackened to a greater or less degree, as far as the end of the field of view of the camera, while the fifth strip was very faint at this limit.

On Plate III(*c*), the prenumbra mentioned above is clearly shown by the third and fourth strips, coming from the sides of the spectrogram adjacent to the numbered scale. Also the fifth strip shows no sign of this region of weak transmission, as was also the case with the fifteenth strip in Plate VI. The shortest wave length recorded on the negative Plate III(*c*), for the most concentrated solution, was 0.541 μ.

The dependence of the limits of absorption upon thickness of layer for the mother solution of copper bromide was shown graphically by Plate VII(*b*). The angle of the wedge-cell was 27′.3 and the depth of solution varied linearly from about 0 to 0.25 mm. In the deeper portions of the cell the solution appeared dull brown. The washed-out band in the blue-green was observed with the eye-piece and, consequently, its presence on the spectrogram is not due to the photographic film alone. As for the chloride of copper, so also for the bromide, the absorption of the ultra-violet is very strong. The shortest wave length recorded on the negative for the least depth of liquid is 3250.5 A. U., and that for the greatest depth is about 0.438 μ; Plate VII(*b*), shows the boundary of the ultra-violet band sufficiently well to make further comment on this region superfluous. The band in the green has its middle at, roughly, 0.518 μ. The fact that the ends of the photographic strips resulting from the 3 successive exposures, which ends are in the vicinity of 0.597 μ, suggest a straight line which slants with respect to the length of the spectrogram, calls attention to the general absorption of the least refrangible portions of the spectrum.

The following facts were obtained by eye observations with the spectroscope, the cell having the same depth as above. The numbers recorded for the limits of transmission in the red for the first, third, fifth, seventh, ninth, eleventh, thirteenth and fifteenth solutions, named in the order of increasing concentration, were 0.750 μ, 0.730 μ, 0.725 μ, 0.720 μ, 0.712 μ, 0.707 μ, 0.690 μ, 0.680 μ, respectively. Since the band in the red has a diffuse end in the visible spectrum, the data just given are useful only in so far as they indicate roughly the progressive increase of absorption with the like variation in concentration, but they are not to be considered as very accurate. The wave lengths of the limits of absorption of the band which extends from the ultra-violet into the visible spectrum, as obtained for the solutions mentioned in the above list, agree qualitatively with those derived from the spectrograms; and since the former are less reliable than the latter, they will not be given here. Special attention, however, was

Plate VI.

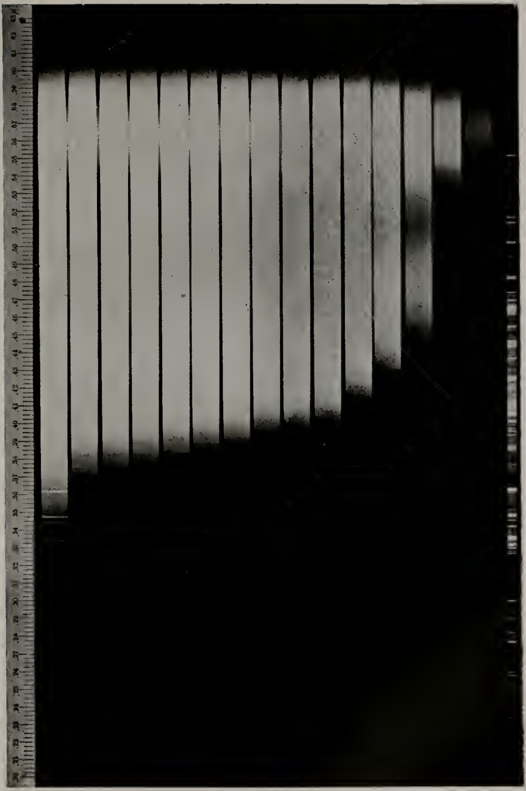

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Plate VII (a).

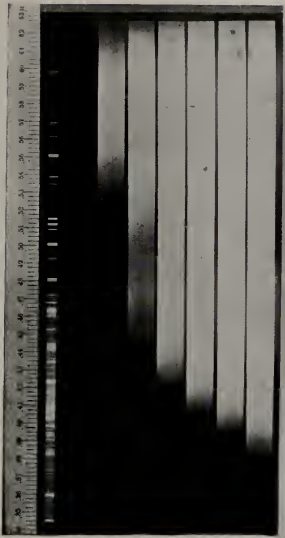
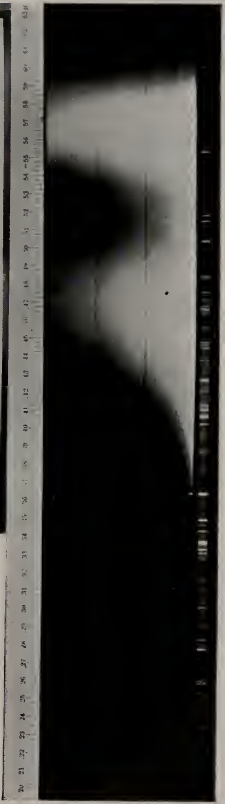


Plate VII (b).



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directed to the solutions of concentration 1.224 and 1.574. in order to find out whether there were any abrupt changes in the absorption of the more concentrated solutions of the series, because the spectrograms of Plates III(*c*) and VI., seemed to indicate a change of this kind. In the spectroscope the solution of concentration 1.224 appeared to transmit a spectrum which commenced at about 0.690 μ, rose gradually to a maximum of transmission, then decreased to about half the maximum intensity near 0.500 μ and, finally, faded away very gradually to zero value in the neighborhood of 0.447 μ. This type of variation in intensity, which is likewise characteristic of the solution of concentration 1.399, is shown correctly by the photographic strip next to the last, both on Plate III(*c*) and on Plate VI., only in so far as a weak prenumbra is indicated for the green and blue, but the eye did not detect a maximum of general absorption followed by slight increase in intensity of transmission as shorter and shorter wave lengths were observed, as would be inferred from the photographic strip in question.

Furthermore, the spectrum of the most concentrated solution of the set began at about 0.680 μ, rose slowly to a maximum of transmission at 0.608 μ, decreased gradually for a certain distance, then fell off rather abruptly near 0.545 μ and, finally, faded away to invisibility in the vicinity of 0.495 μ. The colors which were transmitted clearly enough to be recognized, *i. e.*, bright red, orange, yellow and green, were greatly weakened in intensity as compared with that of the light incident upon the absorbing layer of solution.

The region of very weak transmission between 0.545 μ and 0.495 μ was not shown by the negative from which Plates III(*c*) and VI. were reproduced. The conclusion to be drawn, then, is that there was no abrupt change in the general characteristics of the regions of absorption and of transmission of the several solutions of copper bromide studied, and that the lack of complete agreement between the results obtained, on the one hand by the photographic method, and on the other by observations in the case of the two solutions of greatest concentration, was due to the fact that certain portions of the spectra transmitted were of too feeble intensity to affect the photographic film or plate either at all, or in a correct manner. Thus, the case of copper bromide furnishes a good illustration of the desirability, if not of the necessity, in general, of supplementing photographic work by eye observations.

Cobalt Chloride and Calcium Chloride.—(See Plates VIII., IX(*a*) and IX(*b*), the last two are reduced to three-fourths of the original size.) The spectrogram of Plate VIII. will be first discussed. The concentration of the cobalt chloride in all of the solution is a constant, 0.271. The concentrations of the calcium chloride were 0.000, 1.676, 2.514, 2.724, 2.849, 2.919, 3.007, 3.128, 3.336 and 3.765. These solutions were made up so as to show successive color changes which, judged by the eye, were as uniform as possible. The colors themselves varied from clear red to deep blue, passing through intermediate shades of garnet, purple, violet, etc.

The strip corresponding to the solution that contained no calcium chloride, appears next to the numbered scale, while the strip associated with the solution which had the greatest concentration in calcium chloride, lies closest to the comparison spectrum. The depth of the cell was 1.41 cm.

These regions of absorption are shown by the spectrogram. One of these is in the extreme ultra-violet, another is in the green, and a third is in the orange and red. The solution of cobalt chloride alone was unusually transparent to short waves of light, transmitting the spark line at 2265.1. The negative showed no shorter wave lengths. The band in the ultra-violet gradually extended to longer waves, as the concentration of calcium chloride increased. For example, the ninth solution transmitted the line of wave length 2558.0, but nothing more refrangible, and the continuous background did not persist quite as far as to the spark line last mentioned. The line spectrum of the strip adjacent to the spark scale is not comparable with the other strips, because the Leyden jar broke down in the course of the exposure. This accident had no influence, of course, on that part of the tenth strip, which was obtained by the use of the Nernst filament. The marked lack of intensity of the comparison spectrum was due to the

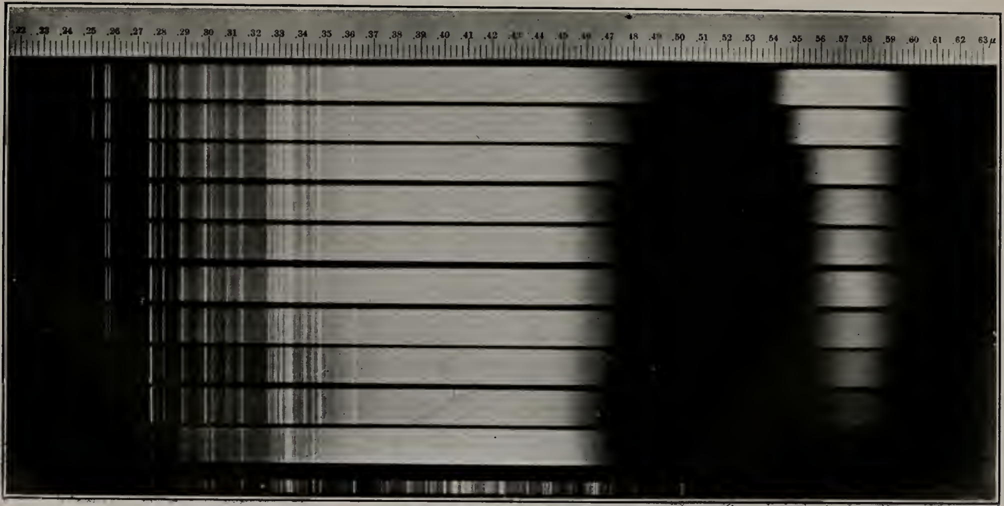
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Plate VIII.

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same break. The band in the green extended from about 0.505 μ to 0.530 μ, as shown by the negative for the solution containing no calcium chloride. This band widened out more and more as the concentration of the calcium chloride increased. At the same time general absorption was present on the orange side of the band, and not on the blue side. This fact, together with the one to be discussed below, in connection with the eye observations, namely, that there were bands of continually increasing width in the red, accounts for the change in the resultant color from red to blue when the calcium chloride was added to the solution of cobalt chloride.

Plate IX(*a*) shows the variation of the absorption of solutions of cobalt chloride and calcium chloride, when the successive increments of concentration were all equal. The electrical conductivities of these solutions were also measured. The constant concentration of the cobalt salt was 0.271 and the concentrations of the calcium chloride were 0.000, 0.325, 0.650, 0.974, 1.299, 1.624, 1.950. The common difference used in the calculation was 0.3248. The concentration of mother solutions of cobalt and of calcium chloride were, respectively, 2.71 and 4.06 N. The solution which contained the greatest amount of calcium chloride has its photographic strip adjacent to the comparison spectrum. The depth of the cell was the same as for Plate VIII.

The region of absorption in the ultra-violet widened out from 2194.7 to about 0.245 μ, when the extreme strips were measured. The limits of the band in the green increased linearly with the like change in the concentration of the calcium chloride. Also the centre of this band remained at the same wave length 0.518 μ for the 7 solutions under consideration.

Plate IX(*b*) gives the absorption spectra of another set of solutions containing the chlorides of cobalt and of calcium. These solutions were made up of such concentrations as to contain the same number of chlorine atoms as the corresponding solutions of a set in which aluminium chloride was the dehydrating agent, instead of calcium chloride. The reasons for this will be discussed later, when the facts about the spectra of aluminium chloride are given. Plate IX(*b*) supplements Plate IX(*a*) from the standpoint of concentrations, and also because of the circumstance that the solutions of both of these spectrograms have their conductivity data collected in one table and in a single curve in a later section. The concentration of the cobalt chloride was 0.271, as before, and the concentrations of the calcium chloride were 0.000, 1.676, 2.091, 2.515, 2.671, 2.830, 3.143, 3.555. Therefore, the differences of first order were 1.676, 0.415, 0.524, 0.156, 0.159, 0.313, 0.412. The depth of the absorbing layer, the times of exposure, and the relative positions of the photographic strips are the same for Plate IX(*b*) as for Plate IX(*a*). The negative for IX(*b*) shows a faint trace of the spark line at 2194.7 and 2573.1 for the strips associated respectively with the solutions of least and greatest concentration in the calcium salt. The continuous background does not extend quite as far as the wave lengths just given, especially in the case of the most concentrated solution. The general absorption in the yellow and orange is brought out clearly by the eighth strip. The question as to how much of the absorption in any given mixture of solutions, is to be ascribed to the colored salt, and how much is due to the dehydrating agent, will be taken up immediately after the other matters pertaining to the solutions containing cobalt chloride, together with calcium chloride, calcium bromide, or aluminium bromide shall have been discussed.

The most important facts brought out by the observations of the bands in the orange and red were the following: It is not necessary to give here the data relative to the band in the green, since they confirm in detail the results obtained photographically, and the latter is shown by the spectrograms.

The solutions studied with the spectroscope were the ones which accompany Plate VIII. The depth of cell used was 2.5 cm. With distilled water in the cell the red end of the spectrum appeared to begin at about 0.775 μ. The solution containing only cobalt chloride, as well as the one having the concentration 1.676, showed no absorption in the red. For the solution of concentration 2.514 of the calcium salt, 2

Plate IX(a).

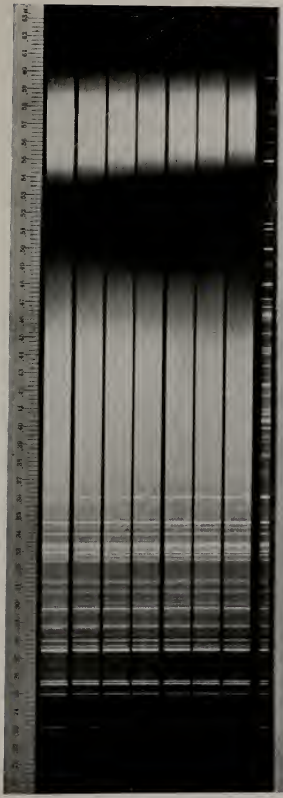
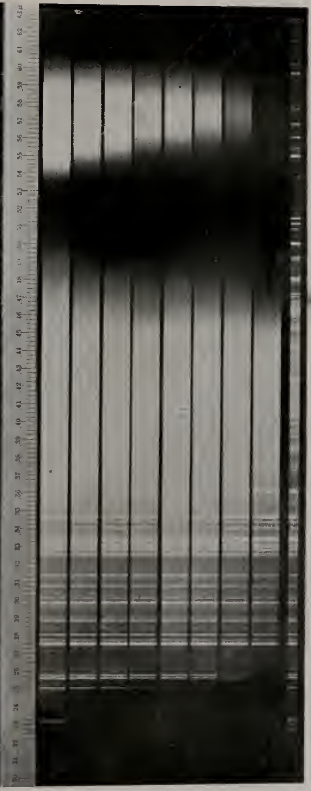


Plate IX(b).



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very faint flutings of intensity showed their maxima of absorption at 0.697 μ and 0.661 μ. By moving the spectrum across the field of view, it was just barely possible to see 2 extremely faint bands which were quite narrow, and which were situated at the shorter wave length side of the band at 0.662 μ. They were too faint, however, to set upon with the cross-hair. The next solution in order of concentration, 2.274, began to transmit faintly at 0.770 μ. The bands at 0.697 μ and 0.661 μ were more intense than before. A faint band appeared at 0.624 μ and a very faint one at 0.609 μ. An extremely faint, narrow band between the two just mentioned, could be seen with great difficulty.

A general idea of the appearance of the successive regions of transmission and absorption, for the solution of concentration 2.849, is given in Fig. 8 (*a*). The abscissae denote wave lengths and the ordinates show estimated intensities of transmission. The centres of the red regions of greatest transparency were, respectively, 0.726 μ and 0.675 μ. One absorption band was at 0.697 μ and the centre of the next band was at 0.661 μ. The entire region from 0.767 μ to beyond 0.660 μ had the appearance of a weak flat band with 2 maxima of absorption, the one at 0.697 μ and the other at 0.661 μ superposed upon it. The absorption at 0.697 μ was more intense than at 0.661 μ. Beyond 0.661 μ the general transmission was uniformly strong, but not as intense as when the cell contained water alone. The narrow band at 6045 was very faint; the next narrow band had the position given by 6245. This band was slightly more intense than the one at 6095. The last 2 bands had about the same width. The spectrum of the solution whose concentration in calcium chloride was 2.919, did not differ enough from that of the solution just discussed to merit further comment. For the solution of concentration 3.007 the band at 0.697 extended from 0.706 μ to 0.686 μ. The bright region lying between the bands at 0.661 μ and 6405 began at 0.655 μ, *i. e.*, the band at 0.661 μ ended rather abruptly at 0.655 μ. In all other particulars the spectrum of this solution was qualitatively similar to the spectra of the two preceding solutions.

The contrasts were more pronounced for the solution of concentration 3.128 than for any of the solutions containing smaller amounts of the dehydrating agent. The spectrum had gradually changed to the form suggested by Fig. 8

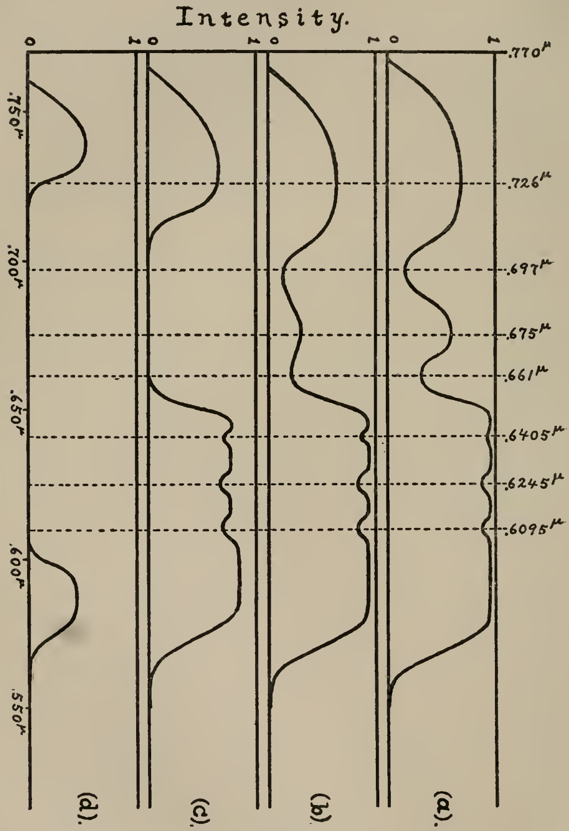

Fig. 8.

(*a*). The maxima of absorption had not changed their wave lengths. The transmission between 0.72 μ and 0.66 μ had become so weak that it was difficult to distinguish the maximum at 0.697 μ.

The bands at 0.697 μ and 0.661 μ had coalesced completely for the solution of concentration 3.336 of the calcium chloride; in other words, the region of weak transmission at 0.675 μ had entirely disappeared [*vide* Plate VIII(*c*) . The resultant wide band extended from 0.714 μ to 0.654 μ with rather abrupt boundaries. The narrow bands at 6245 and 6095 had increased appreciably in depth, and the regions of transmission between 6610, 6405, 6245 and 6095 were much weaker, *i. e.*, the bands were joined by strong general absorption.

The solution which contained the largest amount of the dehydrating agent showed only one intense band in the red [*vide* Plate VIII(*d*)]. This band comprises the interval from 0.724 μ to 0.603 μ. The brightest spot of transmission in the red was at about 0.739 μ. Transmission in the yellow-green was noticeably weakened, and the next region of selective absorption commenced near 0.578 μ, increased to totality at 0.567 μ and then began to fade away again at 0.465 μ. All the spectra of the several solutions seemed to begin at the same wave length, namely at 0.770 μ, *i. e.*, there was no evidence of selective absorption in the extreme red.

The observed freezing points of aqueous solutions containing both cobalt chloride and calcium chloride are tabulated below. Certain associated data are also given, but the interpretation of the tables will be deferred to a later section, in which the general bearing of all the experimental facts on the hypothesis of hydrates will be discussed.

Table I.

1. Concentration of $CoCl_2$ in the mixture.	2. Concentration of $CaCl_2$ in the mixture.	3. Observed freezing-point lowering of the mixture.	4. Lowering of freezing-point if $CaCl_2$ alone were present.	5. Molecular lowering of freezing-point if $CaCl_2$ alone were present.	6. Molecular lowering of freezing-point for $CaCl_2$ in H_2O alone.[1]	7. Column 5 minus column 6.
0.271	0.000	1°.365	. .	. .	. .	. .
0.271	0.162$^{(3)}$	2°.340$^{(5)}$	0°.975	6°.02	4°.92	1°.10
0.271	0.325$^{(3)}$	3°.400$^{(5)}$	2°.035	6°.26	5°.05	1°.21
0.271	0.650$^{(3)}$	6°.130$^{(5)}$	4°.765	7°.33	5°.55	1°.78
0.271	0.974$^{(3)}$	9°.115$^{(5)}$	7°.750	7°.96	6°.29	1°.67
0.271	1.299$^{(3)}$	12°.25$^{(6)}$	10°.88	8°.38	7°.06	1°.32
0.271	1.462$^{(3)}$	14°.00$^{(6)}$	12°.63	8°.64	7°.38	1°.26
0.271	1.624$^{(3)}$	16°.5$^{(6)}$	15°.13	9°.32	7°.88	1°.44
0.271	1.676$^{(2)}$	16°.2$^{(4)}$	14°.83	8°.85	8°.03	0°.82
0.271	1.950$^{(3)}$	23°.0$^{(6)}$	21°.63	11°.09	9°.03	2°.06
0.271	2.091$^{(2)}$	21°.7$^{(4)}$	20°.33	9°.72	9°.32	0°.40
0.271	2.515$^{(2)}$	29°.2$^{(4)}$	27°.83	11°.06	10°.90	0°.16
0.271	2.671$^{(2)}$	34°.5$^{(4)}$	33°.13	12°.40	11°.53	0°.87
0.271	2.830$^{(2)}$	39°.0$^{(4)}$	37°.63	13°.30	12°.32	0°.98
0.271	3.143$^{(2)}$	47°.0$^{(4)}$	45°.63	14°.51	13°.81	0°.70
0.271	3.555$^{(2)}$	?	. .	. .	. .	. .

The solutions whose concentrations are marked (2) or (3) were made up respectively on November 21 and on December 11, 1905. The freezing point lowerings indicated by (4), (5) or (6) were measured on December 7, 1905, February 16 and February 21, 1906. The arithmetical mean of the numbers in the last column, which correspond to solutions for which either 66 or 71 days elapsed between the times when the solutions were made up and when their freezing point lowerings were determined, is 1.48. The like mean for the remaining solutions, which were delayed 15 days, is 0.655. These two numbers show both that the solutions underwent a change with time and that the number of effective particles in the solutions increased, that is, marked hydrolysis took place. Compare, especially, the numbers in the seventh column associated with the concentrations 1.950 and 2.091.

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[1] Interpolated from the table given by Jones and Bassett: THIS JOURNAL, 33, 546 (1905).

The solution of concentration 3.143 was dark blue at room temperature but red near its freezing point. This phenomenon, however, has been observed often before. The most concentrated member of the series tabulated not only turned red, but the salt separated out when an attempt was made to determine its freezing point lowering.

The next table contains the electrical conductivities, at 0°, of the solutions of cobalt chloride and calcium chloride. The data are expressed in reciprocal ohms and reciprocal centimeters.

Table II.

Concentration of $CaCl_2$.	Conductivity.	Concentration of $CaCl_2$.	Conductivity.
0.000	0.02220	1.950	0.10886
0.162	0.03449	2.091	0.10958
0.325	0.04493	2.515	0.11653
0.650	0.06415	2.671	0.11512
0.974	0.07831	2.830	0.11387
1.299	0.09113	3.143	0.10789
1.462	0.09964	3.555	0.09755
1.624	0.10363	. .	. . .

Since the data for the electrical conductivities of standard solutions are usually expressed in terms of the reciprocal of Siemens' mercury unit, at least in books on physical chemistry, it may not be superfluous to explain how the reduction to reciprocal ohms and reciprocal centimeters is effected. The ratio of the Siemens' unit of *resistance* to the ohm is as 1 : 1.063, hence, to change the number representing the value of the *conductivity* of a given solution from reciprocal Siemens' units to reciprocal ohms the number must be multiplied by 1.063. In certain cases the reduction factor is 1.069. Further, reduction to reciprocal centimeters is accomplished by dividing the number expressing the conductivity in reciprocal ohms by the product of one thousand into the "volume" of the solution. For illustration, for 0.02 N aqueous solution of potassium chloride at 25° the conductivity in reciprocal Siemens' units is 129.7; therefore, the conductivity in reciprocal ohms and reciprocal centimeters equals $\frac{129.7 \times 1.063}{1000 \times 50} = 0.002757 = K_s$. Since for one and the same conductivity cell, at the same temperature, the ratio of the specific conductivities of any two solutions is, by definition, equal to the inverse ratio of the ohmic resistances, it is only necessary to determine successively the resistances in the same cell and at constant temperature, of a standard solution and of a solution to be tested, and then to multiply the specific conductivity of the standard solution by the ratio of the ohmic resistance of the standard solution to the ohmic resistance of the solution under investigation, in order to find the value of the specific conductivity of the solution in question. In obvious notation,

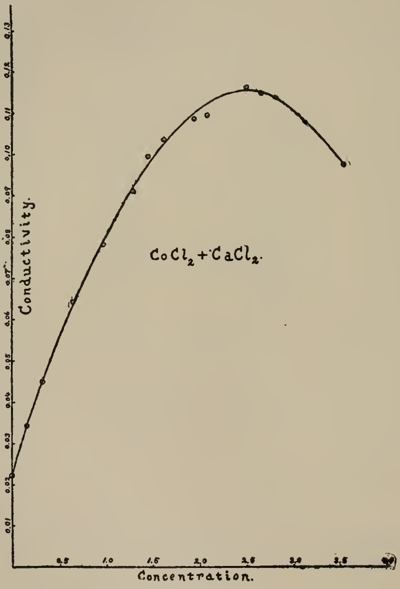


Fig. 9.

$$K_x = K \frac{R_s}{R_x} \text{ohm}^{-1}, \text{ cm.}^{-1}.$$

Fig. 9 shows, graphically, the functional relation between the electrical conductivity and the concentration of the solutions under consideration. The abscissae denote the concentrations of the calcium chloride, and the ordinates give the corresponding conductivities in the units specified above. It is interesting to notice that the conductivity rose to a maximum value and then decreased, as the quantity of the dehydrating agent in the solutions increased. The concentration corresponding to the maximum conductivity was about 2.5. The concentration of the cobalt chloride was the constant 0.271.

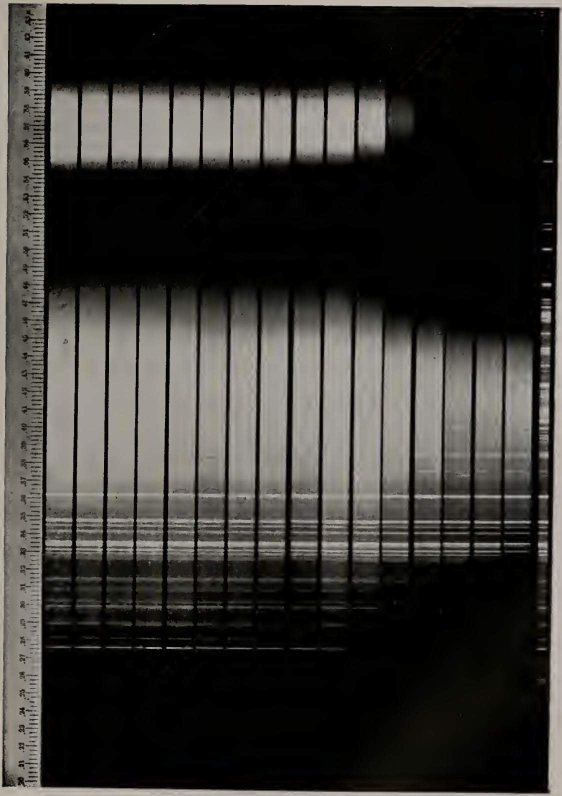
Cobalt Chloride and Calcium Bromide.—(See Plate X. which is reduced to three-fourths of the original size). The cobalt chloride had the concentration 0.271 in all of the solutions of the set now under consideration. The concentrations of the calcium bromide were 0.000, 0.189, 0.379, 0.568, 0.757, 0.947, 1.136, 1.515, 1.893, 2.272, 2.650, 3.143, 3.313, 3.597, 3.938, 4.260. The first 6 increments of concentration were each 0.189, the next 4 separately equaled 0.379, and the remainder had the values 0.493, 0.170, 0.284, 0.341 and 0.322. The concentration of the mother solution of calcium bromide was 4.733. The solutions containing calcium bromide had colors similar to the solutions in which calcium chloride was present, namely, all shades from red to intense blue. The photographic strips succeed one another from the side of the spectrogram adjacent to the numbered scale, to the edge adjoining the spark spectrum, in the order of increasing concentration of calcium bromide. The half-films were not developed simultaneously in this particular case. The depth of the cell was 1.41 cm. The spectrogram shows, qualitatively, the same regions of absorption for the solutions made up with calcium bromide, as had been described above for the solutions containing calcium chloride. The slit of the spectrograph was narrower than usual, and this accounts for the partial absence of continuous background in the ultra-violet. The negative recorded the line at 2265.1 as transmitted by the solution in which no dehydrating agent was present. No shorter wave sensibly affected the film. The region of absorption in the ultra-violet, extended to longer and longer wave lengths as the amount of bromide in the solutions became greater and greater. The shortest wave transmitted by the most concentrated solution, as shown by the negative, had a length of 3261.2 A. U. The middle of the band in the green has approximately the position given by 0.518 μ. The strips pertaining to the first 11 solutions show that the width of the band just mentioned varied almost linearly with the like change in concentration of the calcium chloride. This band, according to the negative for the most concentrated solution, possessed complete absorption from 0.460 μ to wave lengths beyond the nearer end of the spectrogram. The presence of general absorption in the yellow orange is clearly brought out by the photographic strips beginning with the twelfth and ending with the sixteenth.

Eye observations on typical solutions of the set under consideration, were made with the aid of the double cell, and the most important changes in absorption noted were as follows. The comparison of the first and sixth solutions showed no appreciable difference in the orange and red portions of the parallel spectra. The data relative to the band in the green need not be repeated, since they can be obtained in great detail from Plate X.

The sixth and ninth solutions gave spectra of sensibly the same intensity, except in the region of the absorption band in the green. No trace of the bands in the orange and red could be seen in the preceding spectra.

The twelfth solution absorbed the extreme red a little more than the ninth. More specifically, if it be said that the spectrum of the former began at 0.700 μ then the corresponding number for the latter would be 0.736 μ. The narrow bands at 6245 and 6045 (Fig. 8 (*a*)) could only be seen for the twelfth solution, by moving the spectrum across the field of view of the telescope. The axes of the collimator and telescope were fixed at right angles to each other, and the spectrum was moved by rotating the prism by means of the wave length drum.

Plate X.



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The bright regions of transmission were approximately of the same intensity throughout. The thirteenth solution dimmed almost the entire spectrum a little more than the twelfth, and it showed faintly the band at 6405 and more distinctly the bands at 6610, 6245 and 6095. The former solution showed almost complete absorption of all visible light of wave length greater than 0.687 μ. The absorption in the same region was not so intense for the twelfth solution. Both solutions transmitted the violet with about the same intensity.

The fourteenth solution absorbed completely all the red as far as 0.632 μ, thus including the narrow band at 6405. The yellow was much less intensely transmitted by the more concentrated solution than by the weaker one. A change similar in kind, but not in degree, appeared in the indigo and violet.

Only a short, comparatively faint region of yellow was transmitted by the fifteenth solution. If it be stated that the fourteenth solution absorbed everything visible beyond 0.632 μ, then the corresponding number for the fifteenth solution must be 0.619 μ.

The spectrum of the less concentrated solution of the pair was much brighter in the yellow than that of the more concentrated solution.

The most concentrated solution of the series did not transmit the faintest trace of orange or yellow light. Its spectrum extended from about 0.460 μ to the ultra-violet. The intensity of violet transmitted by the fifteenth and sixteenth solutions appeared the same for the 2 spectra.

The freezing point lowerings for the solutions containing both cobalt chloride and calcium chloride are given in the following table:

Table III.

1. Concentration of $CoCl_2$ in the mixture.	2. Concentration of $CaBr_2$ in the mixture.	3. Observed freezing-point lowering of the mixture.	4. Lowering of freezing-point if $CaBr_2$ alone were present.	5. Molecular lowering of freezing-point if $CaBr_2$ alone were present.	6. Molecular lowering of freezing-point for $CaBr_2$ in H_2O alone.[1]	7. Column 5 minus column 6.
0.271	0.000	1°.365	. .	. .	. .	. .
0.271	0.189	2°.703	1°.338	7.09	5.19	1.90
0.271	0.379	4°.276	2°.911	7.68	5.37	2.31
0.271	0.568	5°.627	4°.262	7.50	5.63	1.87
0.271	0.757	7°.600	6°.235	8.24	5.76	2.48
0.271	0.947	9°.732	8°.367	8.84	6.07	2.77
0.271	1.136	11°.25	9°.88	8.70	6.95	1.75
0.271	1.515	15°.0	13°.63	9.00	8.70	0.30
0.271	1.893	21°.6	20°.23	10.69	9.58	1.11
0.271	2.272	29°.5	28°.13	12.38	11.84	0.54
0.271	2.650	40°.0	38°.63	14.58	13.84	0.74
0.271	3.143	56°	54°.6	17.37	16.26[2]	1.11
0.271	3.313	65°	63°.6	19.20	(17.09)[2]	(2.11)
0.271	3.597	65° (?)	. .	. .	. .	. .
0.271	3.938	(?)	. .	. .	. .	. .
0.271	4.260	(?)	. .	. .	. .	. .

The solutions whose concentrations were between 0.189 and 1.136 inclusive of the limits, had their freezing point lowerings determined 74 days after they were made up, whereas the corresponding time for each of the remaining solutions of the series was 14 days. The average value of the first 6 numbers in the last column of Table III. is 2.18, and the mean of the next 5 numbers is 0.76. Hence, the same increase with time of the number of particles which took part in the lowering of the freezing point was observed for the solutions containing both cobalt chloride and calcium chloride, as was pointed out in connection with Table I. for the solutions containing the chlorides of cobalt and of calcium. The solutions having the concentrations 3.143, 3.313 and 3.938 became very viscous jellies near their freezing points and, therefore, it was not possible to determine the temperatures of these points with even a reasonable degree of accuracy. On this account 2 of the numbers in Table III. are enclosed in parentheses. Salt separated out when the attempt was made to ascertain the order of magnitude of the freezing point lowering produced by the most concentrated solution. All of the most concentrated solutions were blue at room temperature, but they were of the characteristic cobalt rose color in the neighborhood of their respective freezing points.

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[1] Interpolated from the table given by Jones and Bassett: THIS JOURNAL, 33, 550 (1905).

[2] Extrapolated.

Table IV. gives the electrical conductivities at 0° of the solutions of cobalt chloride and calcium bromide. As formerly, the conductivity data are expressed in reciprocal ohms and reciprocal centimeters:

Table IV.

Concentration of $CaBr_2$.	Conductivity	Concentration of $CaBr_2$.	Conductivity.
0.000	0.02220	2.272	0.12252
0.189	0.03994	2.650	0.12101
0.379	0.05465	3.143	0.11014
0.568	0.06308	3.313	0.10470
0.757	0.07412	3.597	0.09496
1.136	0.09244	3.938	0.08313
1.515	0.10643	4.260	0.07005
1.893	0.11913	. .	. . .

The dependence of the conductivity upon the concentration of the calcium bromide is shown graphically by Fig. 10. The abscissae denote concentrations of the dehydrating agent and the ordinates give the corresponding conductivities. The concentration of the cobalt chloride was the constant 0.271. The maximum in the curve for the solutions containing the bromide was even more pronounced than it was for the curve pertaining to the solutions of the chloride of calcium. Moreover, these 2 maxima occur at, roughly, the same concentration, *i. e.*, at about 2.5 and 2.4 for the solutions containing the chloride and bromide, respectively.

Cobalt Chloride and Aluminium Chloride.—(See Plates XI(*a*) and XII. The first is reduced to three-fourths of the original size.) The concentrations of the aluminium chloride in the solutions corresponding to Plate XI(*a*) were 0.000, 1.118, 1.394, 1.676, 1.781, 1.887, 2.100 and 2.459. The increments of concentration were 1.118, 0.276, 0.282, 0.105, 0.106, 0.213, 0.359. The concentration of the cobalt chloride throughout was 0.271.

The concentration of the mother solution of aluminium chloride was 2.75. The solutions made up from this mother solution, and containing cobalt chloride, had colors similar to those of solutions in which either the bromide or chloride of calcium was present, namely, all shades from red to intense blue. The photographic strips succeed one another from the side of the spectrogram adjacent to the numbered scale, to the edge contiguous to the spark spectrum, in the order of increasing concentration of the dehydrating agent. The depth of the cell was 1.41 cm. The spectrum shows, qualitatively,

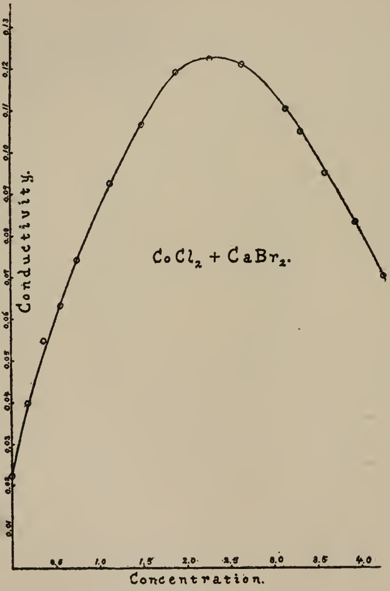


Fig. 10.

the same regions of absorption as have been noted for all of the preceding series or sets of solutions containing cobalt chloride.

The negative recorded the line at 2265.1 as the most refrangible radiation transmitted by the solution which contained none of the aluminium chloride. The most concentrated solution transmitted a trace of the line of wave length 2748.7, but the continuous background was completely absorbed beyond 0.288 μ. The absorption band in the green was at about 0.518 μ. The greatest wave length for light transmitted at the blue side of this band, for the most concentrated solution, was given by the negative as 0.484 μ. The seventh and eighth photographic strips, especially, show general absorption in the orange.

A few attempts were made to find out whether any simple relation might exist between 2 solutions having apparently the same color, the one containing calcium chloride and the other aluminium chloride. Except for the extremely concentrated solution, it was found that, as a first approximation, 2 solutions of the kind just mentioned were isochromatic when they contained equal numbers of chlorine atoms. The number before each comma in the following sequence, denote the concentration of the solution containing the chlorides of cobalt and calcium, and the number immediately following the comma in question signifies the concentration of the corresponding solution containing the same amount of cobalt chloride, and such an amount of aluminium chloride as to possess the same number of chlorine atoms as the solution whose concentration precedes the comma. The pairs are: 1.676, 1.118; 2.091, 1.394; 2.515, 1.676; 2.671, 1.781; 2.830, 1.887; 3.143; 2.100; and 3.555, 2.370. As far as the eye could tell the members of each pair of solutions had the same color when they were viewed in their bottles. All of the calcium chloride solutions and all of the aluminium chloride solutions except the most concentrated one, have their absorption spectra produced by Plates IX(*b*) and XI(*a*), respectively. To make the comparison easier and more direct, the members of the first, third, sixth and last pairs of solutions were photographed side by side and in quick succession. The resulting spectrogram is shown on Plate XII. Counting from the side of the plate nearest to the numbered scale, the first, third, fifth and seventh photographic strips correspond to the solutions which contain calcium chloride, and the remaining strips pertain to the solutions which contain aluminium chloride. The depth of the cell was 1.41 cm. In the ultra-violet the solutions which contained the aluminium salt showed much stronger absorption than those which were made up with the calcium salt. On the other hand, the band in the green is a little more intense for the solutions which contain calcium chloride than for the solutions of the other set. That this difference, however, is not very appreciable is readily seen from Plate XII. Due to the presence of a small quantity of some impurity, the mother solution of aluminium chloride had a slight color in layers of 5 or more cm. in thickness. The facts brought out by the spectrogram of the mother solution of aluminium chloride are given below: Two strips were photographed, the one corresponding to a depth of 15.1 cm. and the other to a depth of 1.41 cm. The Nernst filament was given an exposure each time of 2 minutes and the spark was run for 1.5 min. The negative shows complete absorption of all the ultra-violet and violet as far as 0.415 μ for the deeper layer, and the entire strip is relatively faint and underexposed. In fact, the photographic impression fades away about 230 A. U. farther from the longer wave length end of the negative for the deeper layer than for the shallower one. The faintest trace of the spark line at 2558 was transmitted by the shallow layer of solution; also the line at 2748.7 was barely recorded on the negative. The continuous background bagan at about 0.288 μ and did not attain its full intensity for wave lengths shorter than 0.325 μ. Eye observations completely confirm photographic results in the visible region, especially with regard to appreciable absorption of the violet even for a depth of 5.3 cm., and marked general absorption through the entire spectrum for a depth of 15.1 cm. It was, therefore, evident that the mother solution of aluminium chloride possessed both selective and general

Plate XI(a).

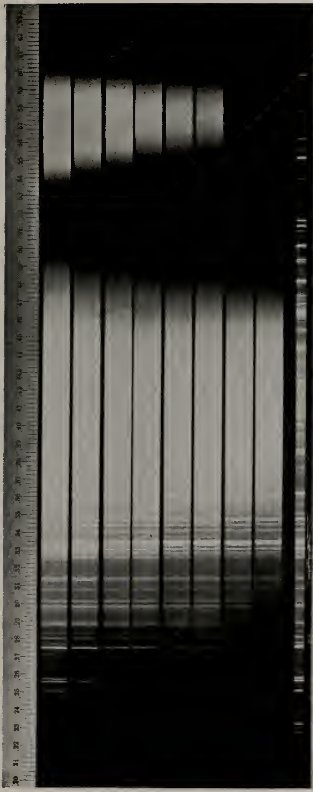
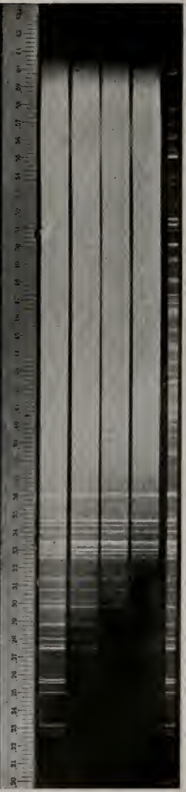


Plate XI(b).



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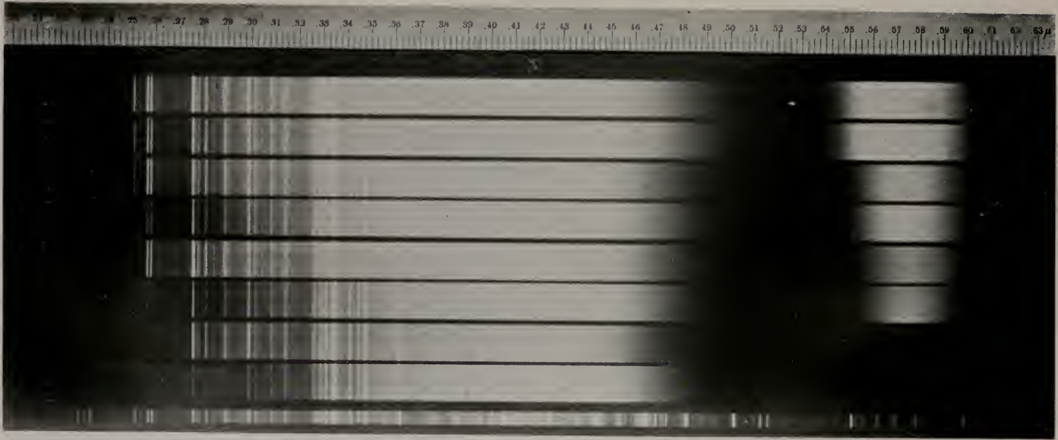

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Plate XII.

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absorption, which were certainly not negligible for long columns of solution, and perhaps not inappreciable for such short columns as 1.41 cm. Consequently, the differences in ultra-violet absorption shown by Plate XII. for the successive pairs of solutions, may be due to the strong absorption in this region of the aluminium chloride, and not to the presence of the cobalt chloride even alone or as influenced by the dehydrating agent.

Before giving the facts obtained by eye observations, by freezing point and conductivity measurements, with the solutions containing the chlorides of cobalt and of aluminium, it may not be out of place to present the salient points brought out by the photographic comparison of the relative intensities and extents of absorption exerted by the mother solution of calcium chloride, calcium bromide and aluminium bromide. The spectra are shown by Plate XI(*b*). The concentration of the calcium chloride solution was 4.51, that of the bromide was 4.236, and that of the aluminium salt was 2.75. The strip nearest to the numbered scale corresponds to distilled water. The next strip pertains to the solution of calcium chloride, the third strip is due to the aluminium chloride, and the strip adjacent to the comparison spectrum is that of calcium bromide. The depth of the cell was 1.41 cm. The negative indicated no absorption at all for the distilled water, in other words, the zinc line at 2024.2 was recorded. The calcium chloride transmitted a trace of the strong cadmium line at 2265.1. This solution absorbed practically all of the continuous background between 0.280 μ and 0.202 μ. The mother solution of aluminium chloride transmitted precisely the same lines as did the solution of calcium chloride, but the former absorbed and weakened the continuous background a good deal more than the latter. When the concentrations of these 2 solutions are taken into account, the relatively great absorbing power of the aluminium salt for the very short waves becomes evident at once. The strong emission line at 2748.7 was weakly transmitted by the solution of calcium bromide, but the continuous background was almost completely absorbed beyond 0.313 μ. Since the concentration of the calcium bromide solution was somewhat less than that of the calcium chloride, the second and fourth photographic strips show, conclusively, how very much stronger the absorption of the bromide is than the chloride for the short light waves. For the depths used in the visible region the 3 solutions in question exerted no appreciable absorption.

In the light of what has just been explained, a comparison of the spectrograms of Plates II., IX(*a*), IX(*b*), X, XI(*a*) and XI(*b*) leads to the conclusion that, in general, the absorption of the ultra-violet light by the cobalt chloride is marked, to some extent, by the superposition of the greater absorption of the dehydrating agent in a given solution. Therefore, the absorption bands in the visible spectrum are better criteria for the behavior of the cobalt salt in the presence of some one of the dehydrating agents than the region of absorption in the ultra-violet. It does not seem necessary to enter into minute details relative to the general principles just stated.

Eye observations on the absorption spectra of the solutions which contained the chlorides of cobalt and aluminium, led to practically the same results as were obtained with the other 2 dehydrating agents under investigation. The chief characteristics of these spectra are shown by the 4 curves of Fig. 8. The depth of column used was 2.5 cm. The solutions of concentration 1.118 and 1.394, in the aluminium salt, did not show even the faintest traces of discrete bands in the red. The entire set of 5 bands could barely be distinguished with the solution of concentration 1.676. The solution of concentration 1.781 has its system of bands represented fairly well by Fig. 8 (*a*) except that the band at 6405 was difficult to see. The bands 6405, 6245 and 6095 were relatively intense, but not very clear cut and well defined for the solution of concentration 1.887. Fig. 8 (*c*) gives an idea of the regions of transmission and absorption for the solution of concentration 2.100. For this solution the bands at 0.697 and 0.661 had coalesced and the resultant region extended from 0.713 μ to 0.653 μ. A deep shadow joined this region to the narrow band at 6405. The bands at 6245 and 6095 were very intense. The width of the band at 6245 was about 55 A. U. A solution which is not included in the set photographed, having the concentration 2.340, showed the entire group of 5 bands as one single region of absorption, like that indicated by Fig. 8. (*d*). This region had the limits 0.724 μ and 0.599 μ. The transmission of light in the interval from 0.599 μ to the beginning of the band in the green was very weak. The most concentrated solution of the series transmitted faintly a narrow band of red. The coalesced group extended from 0.736 μ to 0.590 μ. The region of transmission in the yellow-green was very dim, and lay in the prenumbra of the absorption band whose maximum was near 0.518 μ. The absorption in the red and yellow was much more complete than for the most concentrated member of the series of solutions which contained calcium chloride.

The freezing point lowerings for the solutions containing both cobalt chloride and aluminium chloride are given in the following table:

Table V.

1. Concentration of $CoCl_2$ in the mixture.	2. Concentration of $AlCl_3$ in the mixture.	3. Observed freezing-point lowering of the mixture.	4. Lowering of freezing-point if $AlCl_3$ alone were present.	5. Molecular lowering of freezing-point if $AlCl_3$ alone were present.	6. Molecular lowering of freezing-point for $AlCl_3$ in H_2O alone.	7. Column 5 minus column 6.
0.271	0.000	1°.365	. .	. .	. .	. .
0.271	0.165	2°.692	1°.327	8°.08	5°.72	2.32
0.271	0.330	4°.35	2°.99	9°.06	6°.27	2.79
0.271	0.495	6°.26	4°.80	9°.70	7°.02	2.68
0.271	0.660	8°.71	7°.35	11°.14	7°.80	3.34
0.271	0.825	11°.4	10°.04	12°.17	8°.79	3.38
0.271	0.990	14°.6	13°.24	13°.37	9°.92	3.45
0.271	1.118	17°.5	16°.14	14°.44	10°.84	3.60
0.271	1.394	25°.6	24°.24	17°.39	13°.23	4.16
0.271	1.485	28°.9	27°.54	18°.55	14°.06	4.49
0.271	1.676	38°.0	36°.64	21°.86	15°.95	5.91
0.271	1.781	44°.0	42°.64	23°.94	17°.18	6.76
0.271	1.887	49°.0	47°.64	25°.2	18°.4	6.8
0.271	1.980	54°.0	52°.6	26°.6	19°.7	6.9
0.271	2.096	50 ?	. .	. .	. .	. .
0.271	2.370	. .	. .	. .	. .	. .
0.271	2.459	. .	. .	. .	. .	. .

When cooled by the mixture of ethyl alcohol and solid carbon dioxide the most concentrated solutions became very viscous, red jellies, which either undercooled about 20° and then became solid, or the salt separated out of the jelly. Hence, it was not possible to assign correct values to the freezing point lowerings of these solutions. With the exception of the second or third member, the numbers in the last column of Table V. become gradually larger as the concentration of the solution increases.

The electrical conductivities, together with the corresponding concentrations of the solutions containing cobalt chloride and aluminium chloride, are given in Table VI. The numbers in the second and fourth columns are expressed in reciprocal ohms and reciprocal centimeters:

Table VI.

1. Concentration	2. Conductivity.	3. Concentration.	4. Conductivity.
0.000	0.02220	1.485	0.06657
0.165	0.03845	1.676	0.06076
0.330	0.05050	1.781	0.05830
0.495	0.05924	1.887	0.05468
0.660	0.06577	1.980	0.05054
0.825	0.06889	2.100	0.04747
0.990	0.07078	2.370	0.03736
1.118	0.07204	2.459	0.03279
1.394	0.06887	. .	. . .

The data in the above table are plotted in Fig. 11. The abscissae denote concentration, and the ordinates signify conductivity. The mean curve has a decided maximum like the curves for the solutions containing calcium chloride and calcium bromide. There is this difference, however, between the curves of Fig. 11 and the other 2 curves, namely, that whereas the maximum of the curve associated with aluminium chloride corresponds to a concentration of about 1.1, the maxima for the other 2 dehydrating agents in question occur at the concentration 2.4 and 2.5.

When a sufficient quantity of water is added to a solution of cobalt chloride, which had previously been made blue by the admixture of a solution of some one of the 3 dehydrating agents under investigation, the solution turns back to the characteristic cobalt red. It was thought that by adding water to a chosen solution of the given series, until the color of this solution became practically the same as that of the solution containing a somewhat smaller amount of the dehydrating agent, it might be possible to obtain some facts which would bear a quantitative relation to the hydrates formed in the solutions. If it were possible to take infinitesimal steps these data might be obtained. But, obviously, such a process cannot be realized experimentally. In practice, either one of two difficulties presents itself: (*a*) the successive solutions differ so little in concentration, that the volume of water which has to be added to the more concentrated solution to bring its color to that of the less concentrated one, is too small

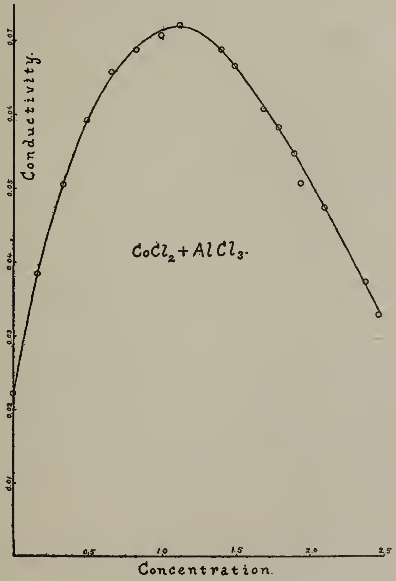
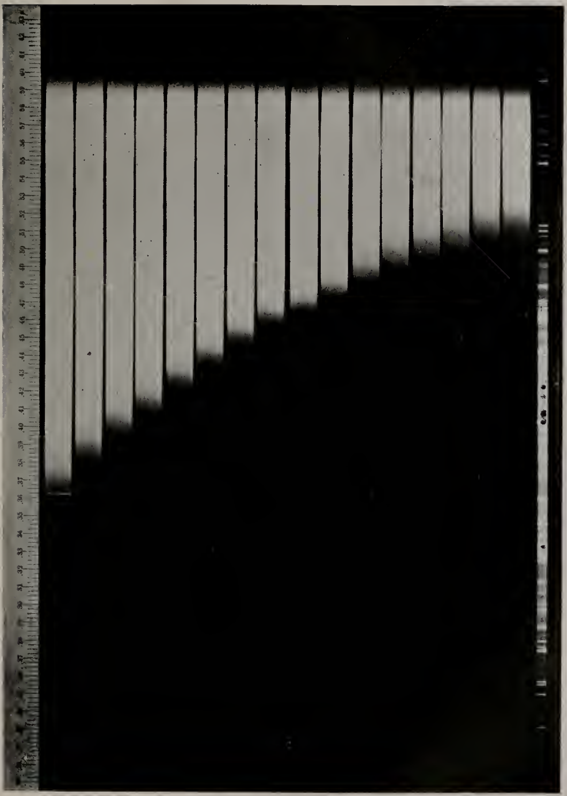


Fig. 11.

to be accurately measured unless undue precautions are taken. Moreover, 2 solutions of nearly equal concentrations differ so little in color as to make the error which necessarily arises in estimating that the colors have been made the same by the act of diluting, relatively great. (*b*) When the concentrations of 2 solutions differ by a reasonable amount, it is not possible to dilute the bluer solution until it assumes the same color as the less blue one, because the volume of water added so greatly increases the volume of the solution as to change the concentration of the cobalt chloride itself, quite independently of any change in the amount of hydration of this salt. In other words, the colors of the 2 solutions cannot readily be made the same under comparable conditions, when the concentrations differ very widely.

The matter under consideration was carefully tested for some of the solutions of cobalt chloride and aluminium chloride, as follows: The lower compartment of a double cell was filled with the less concentrated solution of a chosen pair. A measured volume (4 cc.) of the more concentrated solution was placed in the upper compartment of the cell. Then pure water was run into the upper solution from a burette, until the color in the 2 compartments appeared the same. The upper solution was, of course, made homogeneous. The volumes of water which were both insufficient and too great to dilute the more concentrated solution to the color of the less concentrated were noted, as well as the volume of water which was necessary to produce approximate equality of color. The mean of several trials was taken, In some cases the solutions were examined with the Hilger spectroscope. In this way it was possible to obtain data which are at least of the right order of magnitude. The results are given in Table VII. The first column gives the concentration of the solution to which the water was added. The second column gives in the same line the concentration of the solution which was used as the standard for color. The difference in the concentrations ($c_1 - c_2$) is shown by the third column. The volume (V) of water necessary to produce equality of color

Plate XIII.



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is given in the fourth column. The fifth column gives unit volume of water per unit volume of solution, per unit concentration of aluminium chloride and per unit change in concentration, *i. e.*, $\frac{v}{4c_1(c_1 - c_2)}$.

Table VII.

c_1.	c_2.	$c_1 - c_2$.	v. cc.	$\frac{v}{4c_1(c_1 - c_2)}$.
1.485	1.394	0.991	0.260	0.48
1.676	1.485	0.191	0.470	0.37
1.781	1.676	0.105	0.180	0.24
1.887	1.781	0.106	0.210	0.26
1.980	1.887	0.093	0.145	0.20
2.100	1.980	0.120	0.155	0.15
2.370	2.100	0.270	0.350	0.14

The numbers in the last column show a definite decrease as the concentration of the dehydrating agent increases.

Copper Chloride and Calcium Chloride.—(See Plate XIII., which is reduced to three-fourths of the original size.) The concentration of the copper chloride in all of the solutions had a constant value 0.398. Concentrations of the calcium chloride were 0.0000, 0.271, 0.541, 0.812, 1.082, 1.353, 1.624 1.894, 2.165 2.435, 2.706, 2.977, 3.247, 3.518, 3.788, 4.041. All the increments of concentration have the value 0.2706, except the last one, and its value is 0.253. The concentration of the mother solution of calcium chloride was 4.51. The colors of solutions commenced with clear blue for the most dilute solutions, and passed through the various shades of greenish blue, bluish green, clear green and yellowish green and the concentration of the calcium chloride increased until a deep greenish yellow color was reached.

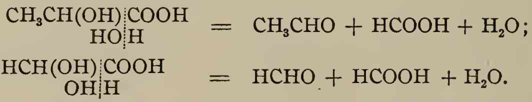
[The remainder of this paper, together with one relating to non-aqueous solvents, will appear in the March number of THIS JOURNAL.]

REPORT.

The Mechanism of Carbon Assimilation in Green Plants.

The nature of the processes whereby, in the sunlight, carbon dioxide is absorbed and oxygen exhaled by green leaves has aroused much interest in recent years. The action occurs on such an enormous scale and is of such prime importance in the organic world, that our very meagre knowledge of the steps involved has been annoying. Two most interesting articles by F. L. Usher and J. H. Priestley[1] have appered recently, which seem to throw much light on this perplexing question.

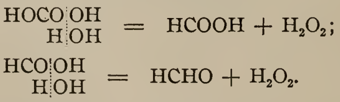
In 1870 Baeyer suggested that formic aldehyde is the first product of the decomposition of carbon dioxide in the plant. In 1877 Erlenmeyer[2] advanced an interesting theory of the mechanism of carbon assimilation. He found that lactic acid, on boiling with dilute sulphuric acid, decomposes into acetic aldehyde and formic acid. Similarly, glycollic acid yields formic aldehyde and formic acid. These reactions may be represented as follows:



$$\begin{array}{r|l} CH_3CH(OH) & COOH \\ HO & H \end{array} = CH_3CHO + HCOOH + H_2O;$$

$$\begin{array}{r|l} HCH(OH) & COOH \\ OH & H \end{array} = HCHO + HCOOH + H_2O.$$

Erlenmeyer believed that the decomposition of carbon dioxide occurs in an analogous way, so that the first products obtained would be formic acid and hydrogen peroxide. He also stated that it was not unthinkable that the formic acid undergoes a similar decomposition, resulting in the formation of formic aldehyde; hydrogen peroxide would have to be produced simultaneously in this change also.



$$\begin{array}{r|l} HOCO & OH \\ H & OH \end{array} = HCOOH + H_2O_2;$$

$$\begin{array}{r|l} HCO & OH \\ H & OH \end{array} = HCHO + H_2O_2.$$

The work of Usher and Priestley agrees in all details with the views of Erlenmeyer. Quite recently Bouilhac and Tréboux have shown that *Elodea* forms starch in the dark from a 0.001 per cent solution of formic aldehyde. Their work demonstrated the extreme toxicity of formic aldehyde.

The authors of the papers under review state that if formic aldehyde is produced, it must be very rapidly transformed into some physiologically inert substance and the hydrogen peroxide must be decomposed with the evolution of oxygen. They show the presence of catalase, the enzyme which decomposes hydrogen peroxide into water and oxygen, in the chloroplasts of plants belonging to 46 Natural Orders. They studied the production of formic aldehyde and the manner of its removal as follows: Since formic aldehyde must be so quickly removed in the living plant, they killed the *Elodea* by boiling it for 30 seconds and then exposed it to sunlight. In a few hours the plants were bleached and on dipping the leaves into a solution of rosaniline, decolorized with sulphur dioxide, a red color developed. This does not occur with the living *Elodea*. They attribute the bleaching of the chlorophyll to the accumulation of hydrogen peroxide, because the catalase is destroyed by the boiling. This experiment proved that the initial step in the assimilation of carbon is independent of living protoplasm and also proved that no enzyme is concerned in this step. It furthermore proved that, in all probability, formic aldehyde is produced. They then showed that exposure to the vapor of chloroform has almost the same effect as boiling, that is, on exposure to sunlight the leaves were bleached and formic aldehyde was again found. The formic aldehyde was further identified by distilling an extract of the leaves and obtaining anhydroformaldehydeaniline and also the tetrabrom derivative of hexamethylenetetramine. The fact that chloroform vapor prevents the polymerization of the formaldehyde proves, according to the authors, that this latter process depends on the vitality of the protoplasm and cannot be caused by an enzyme, as the latter substances are not rendered inactive by chloroform. Thus the first stage of carbon assimilation consists in the formation of formic aldehyde and hydrogen peroxide and this is effected by the chlorophyll and sunlight, independently of living protoplasm and enzymes. The hydrogen peroxide is decomposed into water and oxygen by the enzyme catalase, and if this fails to occur it bleaches the chlorophyll. The polymerization of the formic aldehyde is effected by the living protoplasm, but should this fail to occur, it destroys the catalase. In their second paper they show that by painting a thin layer of gelatin with a benzene solution of chlorophyll, a mechanism is obtained which, on exposure to sunlight, decomposes carbon dioxide into formic aldehyde and hydrogen peroxide. They further show that the white petals of *Saxafraga Wallacei*, which can form starch from very dilute solutions of formic aldehyde, when painted with the solution of chlorophyll in benzene, become capable of forming starch from carbon dioxide in the sunlight. By making the gelatin layer alkaline in the experiments described above, they proved that formic acid is an intermediate product in the reduction of carbon dioxide to formic aldehyde. In this case only formic acid is produced and no formic aldehyde.

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[1] P. Roy. Soc., *B.* **77**, 369; **78**, 318 (1906).

[2] Ber. d. chem. Ges., **10**, 634 (1877).

Finally, they proved the *Elodea* is capable of forming starch from formic acid in sunlight. Also, in this case, oxygen was given off, which proves that hydrogen peroxide must likewise be formed in the reduction, which would follow according to Erlenmeyer's view. For the interesting results of the authors on the decomposition of carbon dioxide by means of uranium compounds, in the sunlight, those interested are referred to the original articles. A. S. LOEVENHART.

REVIEWS.

AMERIKANISCHES HOCHSCHULWESEN. EINDRÜCKE UND BETRACHTUNGEN. VON DR. W. BÖTTGER, Privatdozent an der Universität Leipzig. Leipzig: Engelmann. 1906. pp. 70.

The author of this pamphlet spent a year in this country as Research Associate in the Research Laboratory of Physical Chemistry at the Massachusetts Institute of Technology, and in this pamphlet he gives some of his impressions in regard to the *Hochschulwesen* of this country. Now the *Hochschule* is primarily a university in Germany, and if characterized as a technische *Hochschule* it is a Polytechnic Institute or an Institute of Technology. The methods in the two are quite different, though there are, of course, points of similarity. The question suggests itself: Does experience gained in an Institute of Technology, however excellent that institute may be, especially fit one to write on the conditions existing in the universities? It is not the purpose of this brief notice to discuss Dr. Böttger's book as a whole, but only to call attention to a few points referring mainly to the teaching of chemistry in America. The author says:

"In Amerika sieht man das Ziel des Hochschulunterrichts darin, die Leistungen der Durchschnittsmenschen zu erhöhen, während man bekanntlich in Deutschland das Hauptgewicht darauf legt, dass die Besten zu voller Entwicklung kommen können. Mir scheint, dass dieser Umstand den wesentlichsten Unterschied in den beiderseitigen Ansichten über die Ziele des Unterrichts an Hochschulen bildet."

This statement is largely true so far as the work of colleges and technological institutes is concerned; at least, I believe it to be true. If the author refers to the higher work, the graduate work, of our universities, he is wrong. In this work every effort is made to secure the highest results for the best students. The reason why men who are not of the highest order find their way into the learned professions is that the demand is much greater than the supply.

On pages 30–32 an examination paper in chemistry, intended for candidates for the degree of Ph.D. at the Massachusetts Institute of Technology, is given. The paper is a good one, but hardly typical. It would have been much more instructive to give the examination papers for the degree of Ph.D. set in a dozen of our universities.

Under the head of "Die Organisation des Unterrichts" the illustrations are taken from the catalogue of the Massachusetts Institute of Technology. Again, it should be remarked, the plan of instruction described is not typical of American universities, though no doubt excellent in many respects.

The book will hardly be helpful to Americans, and, though interesting, it will prove somewhat misleading to Germans.

I. R.

RESEARCHES ON CELLULOSE. II. (1900–1905). By C. F. CROSS AND E. J. BEVAN. London, New York and Bombay: Longmans, Green & Co. 1906. pp. xii + 184.

The appearance, about 6 years ago, of the authors' first book on cellulose marked a distinct epoch in the chemistry of that substance As is well known, the services of the authors to the elucidation of the cellulose problem have not been confined to the literary side, their discoveries in the laboratory have been of the first importance in this connection. In such circumstances the publication of the present volume, in continuation of the one just mentioned, will naturally excite great interest and high expectations and it may be said at once that these are amply fulfilled. The book is divided into 3 sections, the first consists of a general résumé and forecast, in 3 chapters. Section II. contains an account of original investigations, in the period 1900–1905, consisting of abstracts of communications by various chemists, followed, in each case, by a critical examination of the matter and results from the point of view of the theoretical forecast of Section I. It is divided into (A) Reactions of Synthesis; (B) Reactions of Resolution and Decomposition. In Section III. is given an account of the technical progress in the cellulose industries and a general forecast of technological developments from the point of view of the matter of Section I. Additional bibliographical notes and 2 indices complete the volume.

Among the many excellences of the book three stand out in special prominence. The valuable criticisms of recent work, in Section II., not only help to place each research in its true perspective, but also suggest and inspire further investigations.

The authors possess, to an extent as rare as it is valuable, the admirable faculty of combining "pure" and "applied" chemistry. Although they never lose sight of the actual, or potential technological importance of a discovery, they are equally successful in keeping in constant view results which appear to be of purely theoretical interest.

Finally, a word of thanks and appreciation must be extended to the authors for their clear and most interesting style, qualities which, unfortunately, are far too rare in scientific books and papers.

The reviewer would like to quote from almost every page of the book in support of his commendations and in illustration of the authors' attitude towards their subject, perhaps the following extracts may be taken as typical ones: "Our main purpose is to establish, at a juncture which we consider to be critical, as it is favorable to progress, the definitely agnostic position which involves the recognition of current views of the constitution of cellulose as inadequate, reopens the matter from a more comprehensive point of view, and reduces all or any interpretations of the experimental quantitative facts to their present actual level of 'theoretical' anticipations of final generalizations. In the next place we desire to state the grounds for a considerable widening of the scope of the investigations which will be necessary for reaching such final generalizations of inclusive and exclusive value. There have been many attempts to solve the problem of the constitution of cellulose in terms of molecular formulæ. These essays postulate 'molecules' as the ultimate reacting units of cellulose, and generally extend the analogies of the 'molecular state' to bodies of this class without, we think, sufficient inquiry as to whether such methods of interpretation are really adequate" (Preface, p. vi.). " * * * cellulose is *essentially an aggregate*; the nature of this aggregate is a present definite object of investigation. It is by no means necessary that our ideas of discrete constituent molecular units apply to aggregates of this class. It is, as we know, generally stated that cellulose is a complex polymeride of a unit molecule of dimensions C_6, and of the general type of the carbohydrates, aldose or ketose. As a matter of fact, this view has not contributed to the progress of research, and its vagueness is seen in the necessity for continually altering the dimensions of the supposed polymeride. Thus, in the case of the nitric esters, which have been more extensively investigated than any other group of derivatives, it has been found necessary to abandon the C_{12} formula (Eder) in favor of the C_{24} formula (Vieille), in order to avoid the formulation of nitrates representing fractional proportions of the assumed ultimate C_6, and later researches invalidate the assumption that the arbitrarily enlarged unit has any final value" (p. 5.) "Instances of this order can be multiplied to show that the progress of research in this (nitric) series of esters is obviously rendering the 'cellulose molecule' a function of the degree of refinement of experimental observations" (p. 45). "A general survey of cellulose technology produces the impression, as we have often had occasion to remark, of a high state of development of these arts, marked by extraordinary refinement of method and an accumulation of exact knowledge which, however, would scarcely rank as 'exact' by comparison with other branches of the science, or in the usual sense of the term as applied to scientific knowledge. We think this arises from the want of a theory, or generalization applicable to the cellulose groups, as to compounds in being, *i. e.*, in action and reaction" (p. 168).

The account given in Section III. of the book, of the present position and recent improvements in the manufacture of artificial silk and of the applications of viscose is brief, but admirably clear and interesting. One more quotation may be given to show the authors' general attitude: "It is not the purpose of this essay to formulate the many objectives of research in terms, nor to anticipate the results of such research. Our aim is to provoke discussion and generally to indicate directions of investigation, which we hope will be undertaken without regard to 'specialists' ' qualifications" (p. 174).

Messrs. Cross and Bevan have placed the chemical world under a decided obligation by the issue of their book and no person who is interested in chemical progress can afford to neglect reading it. J. B. T.

THE PRINCIPLES OF QUALITATIVE ANALYSIS, FROM THE STANDPOINT OF THE THEORY OF ELECTROLYTIC DISSOCIATION AND THE LAW OF MASS ACTION. By WILHELM BÖTTGER, Privatdocent in the University of Leipzig. Translated with the author's sanction and revised with his co-operation by WILLIAM GABB SMEATON, Instructor in General Chemistry in the University of Michigan. Philadelphia: P. Blakiston's Son & Co. 1906. pp. 300. Price, $2.00.

Since the introduction of the study of physical chemistry, and especially since the common acceptance of the theory of electrolytic dissociation, many manuals of qualitative analysis, written avowedly in terms of the dissociation theory, have appeared in this country and abroad. An examination of most of these manuals shows that the changes from the older system are superficial and are generally confined to a brief exposition of the dissociation theory in the introduction, and reference to the precipitation of cations or anions instead of the precipitation of metals or acids, in the text.

This seemingly timid procedure was, however, based on sound reasoning. College students in America usually study qualitative analysis in their second year, in Germany and England in their first. A glance at most text-books of chemistry for undergraduates, written by avowed physical chemists, shows that the authors do not deem it advisable to teach much physical chemistry to the beginner; hence, the undergraduate is not prepared for a thorough application of physical chemistry to analysis.

Dr. Böttger addresses students who are prepared; he assumes that the student has studied Ostwald's "Principles of Inorganic Chemistry" and is studying Ostwald's "Scientific Foundations of Analytical Chemistry." For such students Dr. Böttger has written an admirable book. While special attention has been paid to the law of mass action and the dissociation theory, the author everywhere explains reactions in the light of modern general chemistry.

The book is also valuable for the many new tests for individual cations and for the excellent systematic method of testing for anions through the solubilities of the barium, lead and silver salts. The chapter on the rare elements also deserves notice. as several new methods are introduced. Thus the book is not only interesting, but is a valuable practical manual.

E. R.

LECTURE-NOTES ON CHEMISTRY FOR DENTAL STUDENTS. By H. CARLTON SMITH, PHG., Austin Teaching Fellow in Dental Chemistry and Lecturer on Physiological Chemistry at Harvard University Dental School. First Edition. New York: John Wiley & Sons. 1906. pp. 273. Price, $2.50.

The author states in the preface that the arrangement of this book follows rather closely the lecture course given by him at the Harvard Dental School. The book is divided into 8 parts, as follows: Qualitative Analysis, Dental Metallurgy, Volumetric Analysis, Microchemical Analysis, Organic Chemistry, Physiological Chemistry, Digestion, Urine. The task of presenting these subjects, except in a most superficial way, is certainly a hopeless one. The author emphasizes those matters which are of great practical interest to the dentist. Thus the subject of alloys and amalgams is considered at some length and the recent work of Black and others is presented. The subject of dental cements also receives detailed treatment and the composition of the various cements, including the recently introduced "Enamel Cement," or "Artificial Enamel," is given. Directions are included for a number of experiments to be performed by the student. These are inserted in the text.

The author's style is clear and concise and the book, as a whole, is satisfactory. A. S. L.

PORTLAND CEMENT. By RICHARD K. MEADE. Easton, Pa.: Chemical Publishing Co. 1906. 8vo. pp. viii + 385. Price, $3.50.

Among the several books published in recent years upon Portland cement, none will prove more useful than this volume by one whose personal experience and observation have been so intimately associated with that industry. This book is an enlarged and rewritten edition of the author's well-known "Chemical and Physical Examination of Portland Cement." It opens with an interesting chapter on the history of the industry, followed by a discussion of the chemical composition of cement. Under the head of "Proportioning the Raw Materials," are given the methods of calculating the quantities of limestone and cement rock or shale to be used, from the data furnished by analysis of the materials. Much labor is saved here by the use of graphical methods. In Chapter VII., on Kilns and Burning, is an especially good discussion of the chemical changes and the thermo-chemistry of the cement formation. The chapters of the methods of analysis, both of cement itself and of the raw materials, will have much interest to the general practicing chemist, as well as to those already engaged in cement works. Here are the schemes of cement analysis proposed by the Committee of the New York Section of the Society of Chemical Industry, and that proposed by the Committee of the Lehigh Valley Section of the American Chemical Society. The opinion is expressed that the latter will be more acceptable to those chemists engaged in cement mills, although greater accuracy is conceded to the former. Each is accompanied by valuable foot-note references, and there is a full discussion of both procedures. The "Physical Testing of Cement" is fully treated in Chapters XII.–XVII.; here are given the Standard Specifications reported by the American Society for Testing Materials, in June, 1904, and also a discussion of other methods. Since the standard specifications have been endorsed by most of the associations and societies interested in the use of cement in this country, these methods will doubtless soon supersede all others. The book closes with a chapter on the Adulterations in Portland Cement, followed by an appendix and excellent index. FRANK H. THORP.

MONOGRAPHIEN ÜBER ANGEWANDTE ELEKTROCHEMIE, XXIII BAND. ELEKTROLYTISCHE ALKALICHLORIDZERLEGUNG MIT FLÜSSIGEN METALLKATHODEN, VON DR. R. LUCION. Mit 181 in den Text gedruckten Abbildungen und 7 Tabellen. Halle a. S: Druck und Verlag von Wilhelm Knapp. 1906. pp. 204. Price, M. 9.

Dr. Lucion handles the story of the electrolysis of alkaline chlorides with a liquid metal cathode with the same thoroughness and mastery of the subject which has distinguished the other monographs of this admirable series.

In the first section he treats of the employment of mercury as cathode, and of the advantages and the difficulties connected with its use; he describes 50 patented processes employing the mercury cathode; he gives a historical review of the subject, calculations of experts on the financial side of the methods in practice, and tables of conductivity and specific gravity of solutions of potassium and sodium chloride.

In the second section Dr. Lucion discusses, in a similar manner, the methods employing a cathode of a metal in the fused state. Six processes of this type are described.

In speaking of the theoretical simplicity of the electrolytic methods of making chlorine and alkali hydroxides, the author refers to the expectation of some that in the future the carbonates will be made commercially from electrolytically made hydroxides; others seem to believe that hydrochloric acid will be made from electrolytic chlorine, and have patented processes for this purpose. The author points out the fallacy of such hopes, since thermo-chemical considerations show that it requires more energy to convert alkali chlorides into chlorine and alkali hydroxide, than it does to convert them into carbonate and hydrochloric acid. He says that the development of the electrolytic process depends on the demand of the market for chlorine, and as chlorine is in less demand than alkali hydroxides and carbonates, chemical methods for making the two last-mentioned products will continue in use.

Of the 50 mercury-cathode processes described, but 3 are at present in operation, the Solvay, the Castner, and the Kellner. The two last should be considered as one process, the Castner-Kellner, as the inventors have pooled their methods. The Solvay process is in use in Belgium and in Russia, the Castner-Kellner in England, Austria, and in the United States at Niagara Falls.

Of the 5 patented processes using a cathode of molten metal, that of Acker, using molten lead, is the only one which has proved a commercial success. The works are at Niagara Falls.

In comparing the 2 types, that with fused metal cathode has the advantage of the direct yield of fused alkali hydroxide instead of the aqueous solution of hydroxide in the mercury-cathode processes. It has the further advantage that the energy used is concentrated in a small space. In the Acker process a working unit, using 8000 amperes, 75 horse-power, and yielding 581 pounds (263.5 kilos) of sodium hydroxide per day is a comparatively small electric furnace with 4 carbon anodes. A Castner-Kellner cell, yielding 18 kilos of sodium hydroxide (after evaporation) per day and requiring 3.5 horse-power, is 6 feet long and 3 broad, and 14.3 such cells would be needed to furnish the product of one Acker unit. On the other hand, assuming the figures to be correct, the Castner-Kellner process would require just two-thirds of the energy per unit of hydroxide required by the Acker process.

The author says that economy in energy is by no means the only factor in a successful process, but he does not state definitely that one type is better than the other.

The book is excellently illustrated and printed. E. R.

A TEXT-BOOK OF SANITARY AND APPLIED CHEMISTRY OR THE CHEMISTRY OF WATER, AIR AND FOOD. By E. H. S. BAILEY, PH.D., Professor of Chemistry, University of Kansas. New York: The Macmillan Company. 1906. pp. 345. Price, $1.40.

This work resembles, in a general way, Lassar-Cohn's well-known book, "Chemistry in Daily Life." Its scope, however, is limited to those subjects which are of importance to the maintenance of health and to household economy. The book is divided into 2 parts. One part deals with the atmosphere, fuels, ventilation, lighting, water and its purification, sewage and sewage disposal, soaps, methods of cleansing and disinfection. Part II. deals with foods, beverages and accessories, food value and economy in dietetics. The author assumes that the reader has a fair knowledge of the rudiments of chemistry. The style, however, is clear and simple and is not unnecessarily encumbered with technical terms. Quite a large number of simple experiments are given in the text to illustrate the subjects under discussion.

There is great need for the dissemination of popular knowledge along these lines and we hope that the book will be well received. A. S. L.

COURS DE CHIMIE ORGANIQUE. Par FRED. SWARTS. Paris: A. Hermann. 1906. pp. 669. Price, $3.00.

This is an unusually clear and attractive book. Our French colleagues certainly have the power of clear presentation. It is usually a delight to read a French scientific book. This is a good example and the book can therefore be highly recommended to students and teachers. It is not at all exhaustive; it is rather elementary; so much the better. The Germans are the natural writers of exhaustive books. No one can do it as well, but when it comes to the matter of exposition the French are our masters.

There is one feature of the book that calls for mildly adverse comment. Wherever there are references to the literature, French authors are given precedence. To be sure, there are few references, but in most cases these are to French sources.

As an example of the author's power of clear presentation the chapter on the aromatic series (pp. 428–441) may be taken. The arguments are well stated and due attention is given to every suggestion of value that has been made regarding the constitution of benzene. The essential features of Thiele's theory of partial valences are well stated, and the improvement of the Kekulé formula that is brought about by the introduction of Thiele's conception is also fully recognized.

The discussion of hydrocyanic acid and the cyanides furnishes another good illustration of clear presentation. There is very little of the dogmatic in the author's treatment, though he appears to be a little more confident of the constitutional formula of potassium ferrocyanide (see page 161) than some of us are. In regard to the phenomenon of tautomerism as presented by the cyanides, he says: "It is not necessary to assume that KCN is a mixture of $K—C\equiv N$ and of a small proportion of $K—N\equiv C$. This interpretation does not take account of the fact that the alcoholic iodides give only nitriles when they react with KCN. The most plausible explanation is to assume that KCN takes one or the other tautomeric form according to the reactions into which it enters. Further, this is equally true of HCN itself; but we have not yet isolated the two forms, either in the case of the acid or of the salts. The isolation of the two forms has been accomplished only in the case of the esters."

While the writer of this notice does not profess to have read the book through he has examined it pretty carefully, and has not come across anything that calls for censure. It is one of the most satisfactory books that it has been his pleasure to examine for some time. I. R.

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AMERICAN
CHEMICAL JOURNAL

THE ABSORPTION SPECTRA OF CERTAIN SALTS IN AQUEOUS SOLUTION AS AFFECTED BY THE PRESENCE OF CERTAIN OTHER SALTS WITH LARGE HYDRATING POWER.

BY HARRY C. JONES AND HORACE S. UHLER.

(SEVENTEENTH COMMUNICATION.)

(*Continued from the February number.*)

The photographic strip adjacent to the numbered scale corresponds to the solution which did not contain any of the calcium salt. The second strip corresponds to the solution of concentration 0.271, and so on, until, finally, the strip next to the comparison spectrum pertains to the most concentrated solution in the series. The depth of the cell was 1.41 cm. for the Nernst film and spark. The spark line of shortest wave length recorded by the negative for the most dilute solution was 3436.9, but the continuous background barely extended to 0.347 μ. For the solution of concentration 4.041 transmission is shown by the negative, and began at 0.506 μ. Since the successive differences in concentration of the first 15 solutions are all equal, the spectrogram shows at a glance the dependence of the limit of absorption of the region which included the ultra-violet, upon the concentration of the dehydrating agent. That the locus of the left-hand ends of the photographic strips is, as would be expected, not a straight line, but a decided smooth curve, is very apparent. In fact, the band increased in width at the only measurable end by approximately 160 A. U., as the concentration changed from 0.271 to 0.541; but this limit of absorption only moved by about 65 A. U., as the concentration passed from 3.518 to 3.788. In other words, the less refrangible end of the ultra-violet band seems to tend towards a definite limit, as the concentration of the calcium chloride increased. That this absorption is primarily due to the copper chloride, and not to the ultra-violet band of the calcium salt, as such, follows at once from a consideration of plates III(*b*), V., and XI(*b*), and the remarks on the corresponding pages. The change in color of the solutions from blue to green, with increasing amount of calcium chloride, simply means that the ultra-violet band, which did not encroach upon the visible spectrum in the case of the blue solutions, had advanced into the visible spectrum and absorbed the violet and blue to a greater or less extent in the cases of the green and greenish yellow solutions.

Eye observations of the solutions were made with the aid of the cell having 2 compartments. The data thus obtained for the shorter wave length confirmed, then, in detail all the statements made above and derived from the photographs. Each one of the 16 solutions absorbed the red and orange completely. The more refrangible end of this band moved so gradually to shorter wave lengths, that it was only possible to see a very slight shift when the spectra of 2 consecutive members of the set of solutions were viewed simultaneously, but it was not possible to assign a number to the magnitude of the displacement. The best that could be done was to observe the extreme members of the series at the same time, and to obtain the average shift of the visible end of the band by dividing by 15.

The penumbra of the band in question appeared to have the same intensity at 0.640 μ, for the most dilute solution, as at 0.628μ for the most concentrated solution. Therefore, the mean observed displacement was 8 A. U. When the last-named solution was compared with distilled water, it was observed that the spectrum transmitted by the water had about the same intensity at 0.760 μ as the penumbra for the solution at 0.628 μ. Also, the solution did not transmit any color as completely as the water; *i. e.*, the former possessed appreciable general absorption between the regions of complete extinction of light.

The freezing point lowerings for the solution containing the chlorides of copper and of calcium are given in the following table:

1. Concentration of $CaCl_2$ in the mixture.	2. Concentration of $CaCl_2$ in the mixture.	3. Observed freezing point lowering of the mixture.	4. Lowering of freezing point if $CaCl_2$ alone were present.	5. Molecular lowering of freezing point if $CaCl_2$ alone were present.	6. Molecular lowering of freezing point for $CaCl_2$ in water alone.	7. Column 5 minus column 6.
0.398	0.000	20°.433	—	—	—	—
"	0.271	4°.305	1°.872	6°.91	4°.98	1°.93
"	0.541	6°.109	3°.676	6°.80	5°.32	1°.48
"	0.812	8°.28	5°.847	7°.20	5°.92	1°.28
"	1.082	10°.50	8°.067	7°.46	6°.54	0°.92
"	1.353	13°.10	10°.667	7°.88	7°.18	0°.70
"	1.624	16°.50	14°.07	8°.66	7°.88	0°.78
"	1.894	20°.75	18°.32	9°.67	8°.64	1°.03
"	2.165	26°.00	23°.57	10°.89	9°.75	1°.14
"	2.435	31°.25	28°.82	11°.84	10°.63	1°.21
"	2.706	37°.5	35°.07	12°.96	11°.70	1°.26
"	2.977	44°.0	41°.57	13°.96	13°.05	0°.91
"	3.247	52°.5	50°.07	15°.42	14°.32	1°.10
"	3.518		—	—	—	—

As the temperature of the green and yellow-green solutions decreased, the color became bluer. The solution of concentration 3.247 was very viscous and jelly-like near its freezing point. The freezing point lowerings of the last 3 solutions of the series could not be determined, since the salts separated out when the attempt was made to freeze the solutions.

[1] Interpolated from the results of Jones and Bassett: THIS JOURNAL, 33, 546 (1905).

The electrical conductivities, together with the corresponding concentrations of some of the solutions containing copper chloride and calcium chloride are given in Table IX. The conductivity data are expressed in reciprocal ohms and reciprocal centimeters.

Table IX.

Concentration.	Conductivity.	Concentration.	Conductivity.
0.000	0.02938	1.624	0.08643
0.271	0.04601	1.894	0.08864
0.541	0.05586	2.165	0.08955
0.812	0.06512	3.518	0.07937
1.082	0.07320	3.788	0.07222
1.353	0.08146	4.041	0.06517

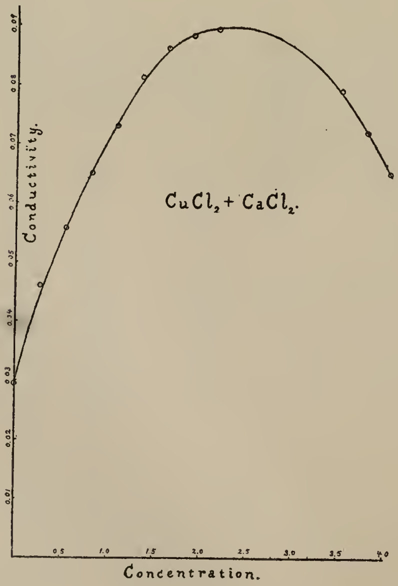

Fig. 12.

The data in the above table are plotted in Fig. 12. The abscissae and ordinates denote, respectively, concentration and conductivity. This curve has a well-defined maximum, just like all the preceding curves.

A peculiar difficulty presented itself when an attempt was made to determine the ohmic resistance of certain of the solutions containing copper chloride, and either calcium chloride or aluminium chloride. The resistance, aside from the cell constant, was first large and then decreased to a definite fixed value. For illustration, the successive resistances of the second solution recorded in the above table were 719.6, 716.9, 703.9, 704.3, 703.8. In all cases, the mean of 3 or more determinations, made after the solution seemed to have reached a steady state, was taken as representing the true ohmic resistance of the solution under investigation. This phenomenon could not be ascribed to changes in temperature, to air bubbles, to absorption of the electrode, or to variable resistance and contact in the electrical circuit. This was shown by repeated and careful tests of all of these matters, as well as of such other causes for the trouble as were thought of from time to time. It was not consistent with the investigation as a whole to pursue this question further.

Copper Chloride and Calcium Bromide.—(See Plates XIV(*a*), XIV(*b*), XV(*a*), XV(*b*), XVI(*a*) and XVI(*b*). Plate XV(*a*) and XV(*b*) is reduced to three-fourths of the original size.) The concentration of the copper chloride in all of the solutions was the constant 0.398. The concentrations of the calcium bromide were 0.000, 0.254, 0.508, 0.763, 1.017, 1.271, 1.525, 2.033, 2.542, 3.050, 3.389, 3.804. The first 6 increments of concentration each equal 0.2542, and the next 3 each equal 0.5084. The one next to the last has the value 0.339, and the last difference equals 0.415. The concentration of the solution of calcium bromide was 4.236. As the concentration of the dehydrating agent increased, the color of the solutions changed from pale blue to deep greenish brown, passing through all intermediate shades of bluish green, clear green and yellowish green. Except in very thin layers, the most concentrated solutions were completely opaque to light. In very thin layers the most concentrated solution was of a dark red color, similar to that of liquid bromine.

Plate XIV(*a*) will be discussed first. The photographic strip nearest to the numbered scale corresponds to the solution which contained no calcium bromide. The solution of concentration 1.271 has its spectrum shown by the strip adjacent to the spark scale. The depth of cell used was 1.41 cm., in order to obtain a spectrogram comparable with the spectrograms for solutions containing copper chloride and dehydrating agents other than calcium bromide. For this depth, however, it was only possible to photograph the first 6 solutions of the series. The spark line of shortest wave length recorded by the negative for the most dilute solution was at 3466.3. The continuous background ceased, however, at about 0.351 μ. The fifth strip on the negative shows very faint transmission from about 0.477 μ to 0.527 μ.

Plate XIV(*a*) gives correctly the details of this strip at the less refrangible side of 0.527 μ. For the sixth solution the negative shows extremely faint transmission from 0.550 μ to 0.581 μ, at which point the sensitivity of the film ceased.

Plate XIV(*b*) gives the spectrogram obtained with the red sensitive photographic plate of the make used throughout the present work. The depth of the cell was 1.41 cm., the same as for Plate XIV(*a*). The strip next to the comparison scales corresponds to the solution of concentration 1.271, while the strip adjacent to the outside edge of Plate XIV(*b*) was acted upon by light that had passed through the solution which contained the smallest mass of calcium bromide. Each exposure to the light from the glower lasted for 2.5 minutes. The fourth strip of the negative in question, which corresponds to the fifth strip of Plate XIV(*a*), shows that transmission began near 0.500 μ and extended to about 1.618 μ. The strip corresponding to the most concentrated solution of the set of 6 solutions now under discussion, showed rather faint transmission from about 0.543 μ to 0.614 μ, with the maximum of intensity at 0.579 μ. It is evident, therefore, that

Plate XIV(a).

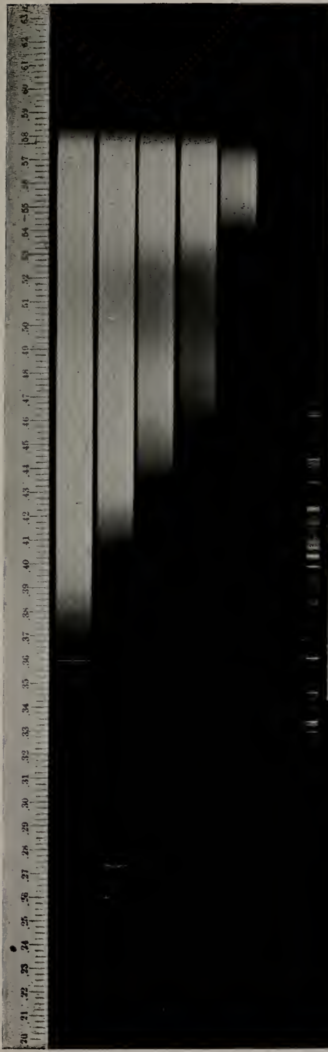

Plate XIV(b).

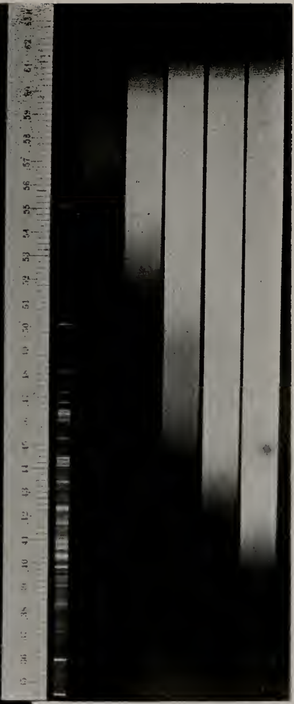

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Plate XV(a).

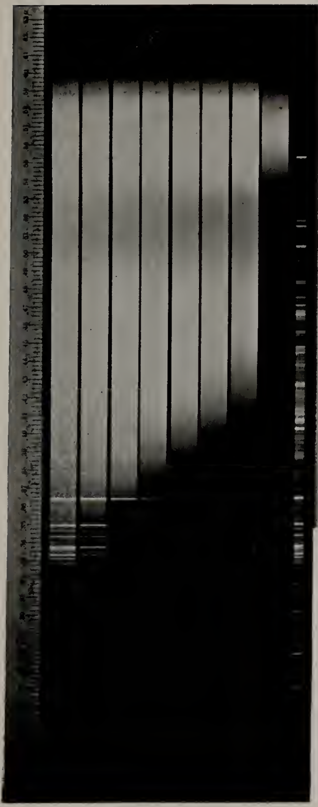
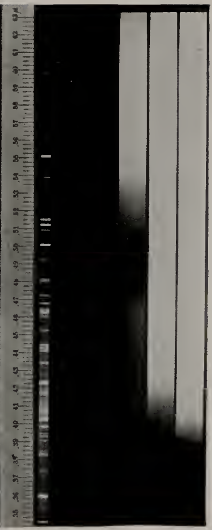


Plate XV(b).



the relative intensities of the region of transmission as recorded by the fifth strip of Plate XIV(*a*), are somewhat exaggerated by the peculiarities of the photographic film. Plate XIV(*b*) shows the presence of true absorption in the red.

The next spectrogram to be considered is that of Plate XV(*a*). The first 8 solutions of the complete set have their absorption spectra shown by this plate. When a sheet of rough white paper, in the daylight, was viewed through the cell and the liquid contained in it, the following colors were observed for the several solutions: The first 2 had no color, the third was faint green, the fourth and fifth were each of a delicate greenish yellow color, the sixth was a decided yellow-green, the seventh was brown, and the eighth was a dull coffee-brown. The photographic strips corresponding, respectively, to the solutions of concentration 0.000, 2.033 in the calcium bromide, are adjacent to the numbered scale and to the spark spectrum. The depth was only 0.08 cm. The strong cadmium line, at wave length 2980.8, was the most refrangible radiation recorded by the negative for the first solution of the series. The continuous spectrum did not extend beyond 0.305 μ. For the seventh solution transmission began at about 0.400 μ. The negative strip for the eighth solution recorded very faint transmission from 0.436 μ on in the direction of greater wave lengths. A minimum was at 0.518 μ, and strong transmission began in the neighborhood of 0.527 μ. As often emphasized in preceding paragraphs, great care must be taken to avoid drawing false conclusions from photographic records for which unavoidable underexposure permitted the variations in sensibility of the photographic emulsion to exert undue influence on the record.

The absorption spectra shown by Plate XV(*b*) pertained to the sixth, seventh, eighth, ninth and tenth solutions of the complete set now under discussion. The photographic strip farthest away from the comparison scales corresponds to the most dilute solution of the group whose spectra are given by the plate. The depth of the cell was 0.08 cm. The glower exposures were each 2.5 minutes long. The negative strip corresponding to the most dilute member of this group of 5 solutions, showed that transmission began very weakly near 0.380 μ. It indicated no general absorption in the orange. The third strip, *i. e.*, the one pertaining to the solution of concentration 2.033, showed on the negative that faint transmission began at 0.434 μ, rose to a maximum at 0.462 μ, then faded out to a minimum of almost complete absorption at 0.495 μ and, finally, became strong at about 0.53 μ and so continued to the end of the negative. The fourth strip, which pertained to the solution of concentration 2.542, showed very faint transmission from 0.568 μ to the end of the negative. The negative recorded nothing for the solution of concentration 3.050.

Plate XVI(*a*) gives the absorption of the solution which contained the largest amount of calcium bromide, of concentration 3.804, when placed in the wedge-shaped cell. The liquid prism showed a dark, reddish-brown color. The edge of the spectrogram nearest to the comparison spectrum corresponds, of course, to the least thickness of absorbing layer. The angle of the wedge was about 15′.6 and, therefore, since the cell was adjusted to begin at zero depth, the greatest thickness of absorbing layer was about 0.14 mm. The negative recorded the strong line of wave length 2265.1 as transmitted by the thinnest portions of the solution, but nothing more refrangible. The continuous background did not extend to shorter radiations than 0.233 μ. The ultra-violet absorption is seen to be intense when the very small thickness of the solution is taken into account. The opacity of the solution began to decrease in the neighborhood of 0.346 μ, and rose gradually to a minimum at 4525. The negative recorded the maximum of absorption in the green as at wavelength 0.515 μ. The spectrogram just referred to is supplemented by Plate XVI(*b*). The negative of which this plate is a reproduction was made with a Cramer trichromatic plate. The solution used was the same as for Plate XVI(*a*). The angle of the cell was about 11′.7, and the absorbing layer varied linearally in depth from zero to 0.11 mm. Each of the 3 successive exposures with the Nernst glower had a duration of 2 minutes. The contour of the regions of absorption were es-

Plates XVI(a).

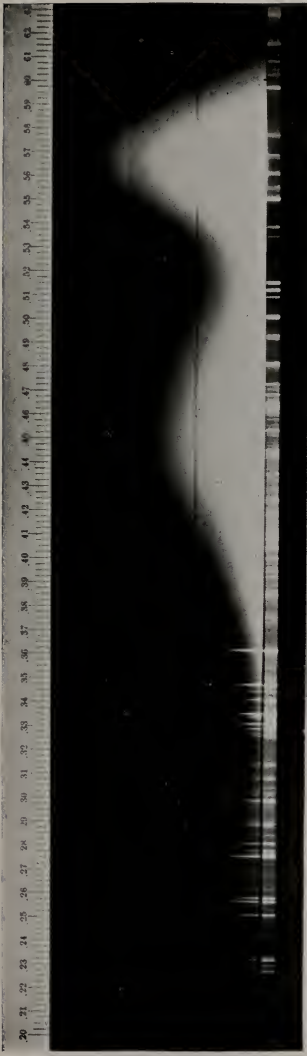
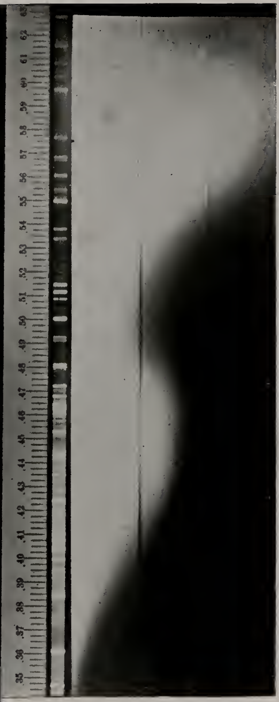


Plate XVI(b).



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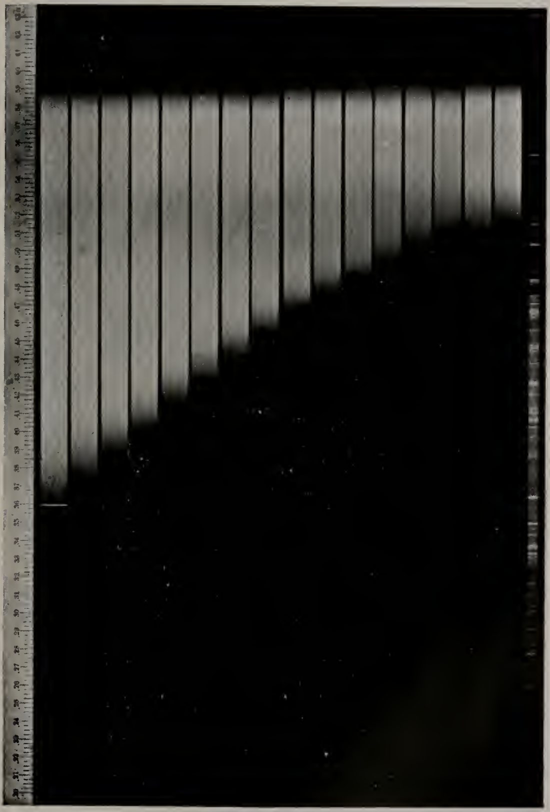
sentially the same as recorded by the negative of Plate XVI(*b*), as by the film of Plate XVI(*a*). Both emulsions gave the wave length 4525 for the more refrangible minimum of absorption. The maximum of absorption for the band in the green was at 0.500 μ, according to the trichromatic plate. Therefore, the 2 spectrograms differed by about 150 A U. in the wave lengths which they give for the absorption band in the green. Since this band is wide and diffuse, it is fair to assign the number 0.508 μ as the approximate position of the middle of the band. Plate XVI(*b*) shows correctly the presence of weak general absorption in the red. The spectrograms for the wedge-shaped layers of solution proved beyond question that the band in the green, as indicated by Plates XIV(*a*), XIV(*b*) and XV(*a*), for the more concentrated solutions, had actual existence and was not due solely to the weak regions of sensibility of the photographic emulsions. The 2 spectrograms of Plates XVI(*a*) and XVI(*b*), by being placed side by side, will illustrate with unusual clearness the part which the photographic plate can play in producing spurious results. This is especially noticeable in the region of the spectrum between 0.55 μ and 0.63 μ.

To serve as a check on the data obtained by the photographic method, as well as for the sake of greater completeness, eye observations were made on the spectra of several of the solutions. The cell with the upper and lower compartments was used, hence the length of the absorbing layer was 2.5 cm. for each solution. The solution of concentration 0.254 of calcium bromide, absorbed the red only a little more than the solution which contained none of this dehydrating agent. These 2 solutions transmitted the yellow and green with equal intensity, at least as far as the eye could tell. The more concentrated solution absorbed almost all the violet, whereas the less concentrated one readily transmitted that color. This accounts for the fact that the former solution appeared bluish green in the cell, whereas the latter had a clear blue tint. The solution of concentration 0.508 absorbed the red just a little more than the one of concentration 0.254. The change was too small to admit of quantitative determination with the dispersion used. For both solutions faint transmission began in the neighborhood of 0.639 μ. The yellow and green are not as bright for the more concentrated solution as for the less concentrated one. Also, the former absorbed considerably more of the blue than the latter. Quantitatively, the same changes were observed when the spectrum of the solution of concentration 0.763 was compared with that of the solution of concentration 0.508. The stronger solution of this pair cut off almost all of the blue and very appreciably weakened the green.

The next solution of the series, of concentration 1.017, absorbed the red a little more than the solution of concentration 0.763. The stronger solution exerted marked general absorption on all the light transmitted, and it absorbed completely all the blue and green as far as the beginning of the yellow-green. If the extreme limits of the regions of transmission for the more concentrated solution be given roughly by 0.630 μ and 0.508 μ, then the corresponding wave lengths for the less concentrated solution would be, respectively, 0.636 μ and 0.468 μ.

The solution which contained the greatest amount of calcium bromide of concentration 3.804, was completely opaque to all visible light in layers of 0.93 depth. A layer 0.12 cm. thick, transmitted, weakly, a narrow band of red extending from about 0.716 μ to 0.653 μ. Red alone was transmitted by a layer of this solution only at 0.06 cm. in thickness. When placed in the wedge-shaped cell, the solution showed very distinctly the 2 bands given by Plates XVI(*a*) and XVI(*b*), *i. e.*, the one in the blue-green and the other in the violet and ultra-violet. So very intense was the absorption of the solution in question, that when a little of it was poured on a plane, parallel piece of quartz, and allowed to drain off with the quartz placed vertically in front of the slit of the spectroscope, the band in the blue-green could be seen distinctly. The results of the freezing point determinations for the solutions which contained copper chloride and calcium bromide are given in Table X. The dark green solu-

Plate XVII.



tions became much lighter in color when they were cooled down in the neighborhood of their freezing points.

The electrical conductivities of the solutions in question were not determined.

Table X.

1. Concentration of $CuCl_2$ in the mixture.	2. Concentration of $CaBr_2$ in the mixture.	3. Observed freezing-point lowering of the mixture.	4. Lowering of freezing-point if $CaBr_2$ alone were present.	5. Molecular lowering of freezing-point if $CaBr_2$ alone were present.	6. Molecular lowering of freezing-point for $CaBr_2$ in H_2O alone.[1]	7. Column 5 minus column 6.
0.398	0.000	2°.433	—	—	—	—
"	0.254	4°.250	1°.817	7°.15	5°.22	1°.93
"	0.508	6°.480	4°.047	7°.97	5°.58	2°.39
"	0.763	8°.660	6°.227	8°.16	5°.65	2°.51
"	1.017	11°.325	8°.892	8°.74	6°.40	2°.34
"	1.271	14°.40	11°.97	9°.42	7°.59	1°.83
"	1.525	18°.25	15°.82	10°.37	8°.71	1°.66
"	2.033	28°.0	25°.57	12°.58	10°.42	2°.16
"	2.542	40°.0	37°.57	14°.78	13°.31	1°.47
"	3.050	56°.0	53°.57	17°.56	15°.80	1°.76
"	3.389	?	—	—	—	—

Copper Chloride and Aluminium Chloride. (See Plate XVII, reduced to three-fourths of the original size.) The concentrations of the mother solutions of the copper and aluminium salts were, respectively, 3.976 and 2.75. The several solutions of the series had the following concentrations of aluminium chloride: 0.000, 0.165, 0.330, 0.495, 0.660, 0.825, 0.990, 1.155, 1.320, 1.485, 1.650, 1.815, 1.980, 2.145, 2.310, 2.482. The successive differences in concentration were all equal to 0.165, except the last, which equaled 0.172. The solutions varied in color from pure blue, through various intermediate shades of greenish blue, bluish green, and clear green, to greenish-yellow. The photographic strip next to the numbered scale corresponds to the solution which contained only copper chloride, and the successive strips, of course, became shorter and shorter as the amount of dehydrating agent in the corresponding solutions increased. The depth of the cell was 1.41 cm.

[1] Interpolated from the table given by Jones and Bassett: THIS JOURNAL, **33**, 550 (1905).

The half-films were not developed simultaneously. The last 2 strips, corresponding to the most concentrated solutions, are not quite comparable with the first 14, as is shown by the fact that they extend a little too far out towards the red end of the spectrum. This was due to opening the slit of the spectrograph a little too widely, as the result of an accidental blow to the micrometer head and the failure to produce exactly the original adjustment.

The negative for the first strip recorded very faintly the intense cadmium line of wave length 3403.7, but nothing more refrangible. The continuous background, however, barely extended to 0.347 μ. According to the negative the most concentrated solution began to transmit at 0.504 μ.

Since the concentrations of the aluminium chloride are in arithmetical progression, the spectrogram shows at a glance the fundamental relation between the limit of absorption of the shorter waves and the concentration of the solution. That the curve of absorption advanced rapidly along the wave lengths at first, and then changed by smaller steps, is shown by the fact that about 150 A. U. lie between the more refrangible ends of the third and fourth photographic strips, whereas only 50 such units are comprised in the corresponding interval between the fifteenth and sixteenth strips.

The solutions were studied in pairs, with the aid of the spectrograph and double-compartment cell. The data obtained visually for the limits of absorption in the violet and blue, agree completely with the photographic results and, therefore, they will not be repeated. Each solution absorbed the red a little more than the one immediately preceding and, hence, the less concentrated member of the set.

The dispersion of the spectroscope was not great enough in this region to enable the observer to obtain quantitative results for consecutive solutions. The most dilute solution began to transmit red at about 0.644 μ, and the most concentrated had, approximately, the same intensity of transmission at 0.629 μ. Therefore, since there were 16 solutions and 15 increments of concentration, the average increase in absorption in the red was 10 A. U. Judged by the eye, the extreme solution of the series transmitted the yellow-green with the same intensity.

The solution of concentration 2.482 of aluminium chloride, was compared with some of the solutions which contained copper chloride and calcium chloride. It was found that the solution having the concentration 3.788 of calcium chloride, had almost identically the same region of transmission as the most concentrated solution of the set containing aluminium chloride.

The cryoscopic data for the solutions which contained the chlorides of aluminium and copper are given below in Table XI:

Table XI.

1. Concentration of $CuCl_2$ in the mixture.	2. Concentration of $AlCl_3$ in the mixture.	3. Observed freezing point lowering of the mixture.	4. Lowering of freezing point if $AlCl_3$ alone were present.	5. Molecular lowering of freezing point if $AlCl_3$ alone were present.	6. Molecular lowering of freezing point for $AlCl_3$ in H_2O alone.[1]	7. Column 5 minus column 6.
0.398	0.000	2°.433	—	—	—	—
"	0.165	3°.900	1°.467	8°.89	5°.72	3°.17
"	0.330	5°.740	3°.307	10°.02	6°.27	3°.75
"	0.495	7°.850	5°.417	10°.94	7°.02	3°.92
"	0.660	10°.325	7°.892	11°.96	7°.80	4°.16
"	0.825	13°.3	10°.87	13°.18	8°.79	4°.39
"	0.990	17°.0	14°.57	14°.72	9°.92	4°.80
"	1.155	21°.8	19°.37	16°.77	11°.11	5°.66
"	1.320	27°.0	24°.57	18°.61	12°.55	6°.06
"	1.485	32°.5	30°.07	20°.25	14°.04	6°.21
"	1.650	38°.8	36°.37	22°.04	15°.65	6°.39
"	1.815	46°.5	44°.1	24°.30	17°.57	6°.73
"	1.980	55°.5	53°.1	26°.82	19°.50	7°.32
"	2.145	66°.0	63°.6	29°.65	21°.43	8°.22
"	2.310	?	—	—	—	—

The electrical conductivities, together with the corresponding concentrations of the solution containing copper chloride and aluminium chloride, are given in Table XII. The numbers in the second and fourth columns are expressed in reciprocal ohms and reciprocal centimeters:

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[1] Interpolated from the table given by Jones and Getman: Z. physik. Chem., 49, 422 (1904).

Table XII.

Concentration of $AlCl_3$.	Conductivity.	Concentration of $AlCl_3$.	Conductivity.
0.000	0.02996	1.485	0.05917
0.165	0.04264	1.650	0.05504
0.330	0.05312	1.815	0.05028
0.495	0.05834	1.980	0.04584
0.660	0.06150	2.145	0.04054
0.990	0.06366	2.310	0.03486
1.155	0.06400	2.482	0.02924
1.320	0.06273	—	—

The data of the last table are shown graphically by Fig. 13. The abscissae denote concentrations of aluminium chloride, and the ordinate give the corresponding conductivities of the solution. This curve has a marked maximum like all the 4 preceding curves. Moreover, the concentration asso-

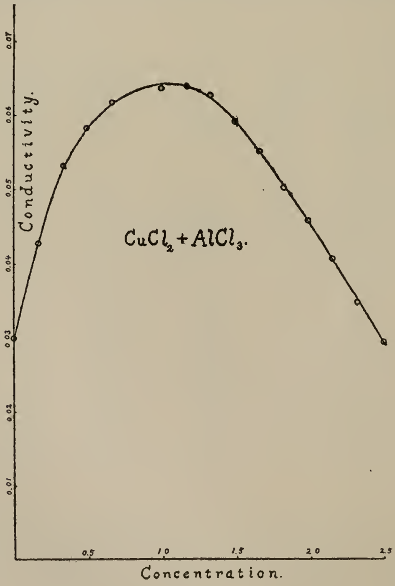


Fig. 13.

ciated with the maximum of conductivity in question, has the value 1.1, and this is exactly the same value as was found for the corresponding point of the curve pertaining to the solutions which contained cobalt chloride and aluminium chloride.

Copper Bromide and Calcium Chloride.—(See Plate XVIII(*a*) and XVIII(*b*), reduced to three-fourths of the original size.) The concentrations of the mother solutions of copper bromide and calcium chloride were, respectively, 2.186 and 4.51. The concentrations of the calcium chloride in the solutions, whose absorption spectra are given by the plates designated above, were: 0.000, 0.451, 0.902, 1.353, 1.804, 2.255, 2.706, 3.157, 3.608 and 4.059. The successive differences in concentration were all equal to 0.451. The concentration of the copper bromide in all the solutions had the constant value 0.219. By transmitted daylight the solutions, in columns 2.5 cm. long, had colors which varied from greenish blue, through various shades of green and brownish green, to dark reddish brown. The photographic strip nearest to the number scale of Plate XVIII(*a*) corresponds to the solution which contained only the one salt. The remaining strips succeed one another in the order of increasing amounts of calcium chloride in the solutions, so that the strip adjacent to the comparison spectrum pertains to the solution of concentration 0.059. The depth of the cell was 1.41 cm. The times of exposure for the Nernst glower and spark were, respectively, 90 seconds and 80 seconds. The line of demarkation of the half-films lies between the fifth and sixth photographic strips, counting either way.

Of the various facts brought out by the negative for Plate XVIII(*a*), the following are the more striking: In the most dilute solution transmission began at 0.377 μ, the second photographic strip began at 0.382 μ. On the negative the fourth and fifth strips commenced at about 0.419 μ and 0.499 μ, respectively. Consequently, when the concentration of the calcium chloride was changed from 0.000 to 0.451, the end of the absorption band in the ultra-violet and violet was displaced towards the red by 50 A. U. Again, when the concentration of the dehydrating agent varied from 1.353 to 1.804, the above-mentioned end of the absorption band was displaced by 300 A. U. in the same direction. Therefore, as is easily seen from the spectrogram, up to a certain concentration the end of the band encroached more rapidly on the region of longer waves, as the concentration of calcium chloride increased. In all the cases discussed in the preceding pages, the successive increments of absorption decreased steadily as the concentration of the dehydrating agent increased in arithmetical progression. As just noted, the change is exactly the reverse for the solutions of copper bromide and calcium chloride. With the sixth photographic strip the end of the absorption band altered somewhat its nature. The negative showed that very weak transmission began at about 0.478 μ, and extended over a relatively wide range of wave lengths. In fact, comparatively intense transmission began only near 0.528 μ. The negative strip corresponding to the most concentrated solution showed that transmission was weak and began in the neighborhood of 0.522 μ.

The negative of which Plate XVIII(*b*) is a reproduction, was taken with a Cramer trichromatic plate. The photographic strip adjacent to the scales corresponds to the most concentrated solution of the set, and the strip at the opposite side of the spectrogram corresponds to the solution of concentration 2.55. The depth of the cell was 1.41 cm. Each exposure to the light from the Nernst filament was 2 minutes in length. The negative strip last mentioned showed that faint transmission began near 0.485 μ, and continued weak to about 0.494 μ. The apparent lack of agreement between the sixth strip of Plate XVIII(*a*) and the fifth strip of Plate XVIII(*b*), is due as much to the difference in length of the respective exposures as to the peculiarities of the photographic emulsion. Plate XVIII(*b*) recorded the beginning of transmission as at wave length 0.552 and this is exactly the same as was obtained from the negative of Plate XVIII(*a*).

Eye observations were made on the solutions in pairs, with the aid of the two-compartment cell. The results obtained

Plate XVIII(a).

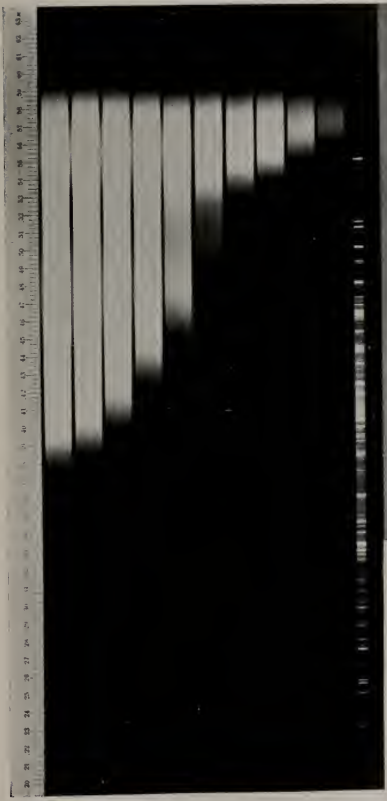
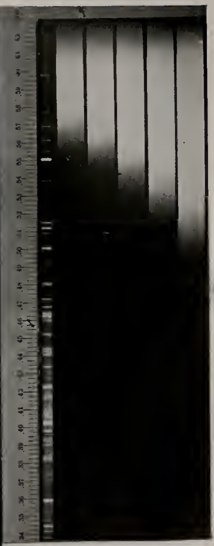


Plate XVIII(b).



by the spectroscope confirmed in detail those derived from the negative. It was noted, especially, that the successive increments of absorption of the band in the violet at first increased with the like change in concentration, and then decreased for the most concentrated solutions. The band in the red extended to the shorter wave lengths by such small increments, when the passage from one solution to its more concentrated successor was made, that it was only possible to obtain the average value of this displacement. Transmission of equal intensity for the most concentrated solution, and for the one which contained no calcium chloride, began at 0.647 μ and 0.667 μ, respectively. Since there were 9 differences in concentration, the average value of the shift of the end of the band in the red was about 22 A. U. When the spectrum of the most dilute solution was compared with that of distilled water, it was observed that the former lacked the deep red and the bright red, and began in the orange-red. These 2 spectra, in the order named, appeared to commence, respectively, at 0.663 μ and 0.772 μ.

The freezing point lowerings of the solutions containing copper bromide and calcium chloride are given in Table XIII:

Table XIII.

1. Concentration of $CuBr_2$ in the mixture.	2. Concentration of $CaCl_2$ in the mixture.	3. Observed freezing point lowering of the mixture.	4. Lowering of freezing point if $CaCl_2$ alone were present.	5. Molecular lowering of freezing point if $CaCl_2$ alone were present.	6. Molecular lowering of freezing point for $CaCl_2$ in H_2O[1] alone.	7. Column 5 minus column 6.
0.219	0.000	1°.200	—	—	—	—
"	0.451	4°.090	2°.890	6°.41	5°.20	1°.21
"	0.902	7°.620	6°.420	7°.12	6°.12	1°.00
"	1.353	11°.70	10°.50	7°.76	7°.18	0°.58
"	1.804	16°.95	15°.75	8°.73	8°.38	0°.35
"	2.255	24°.5	23°.3	10°.33	10°.03	0°.30
"	2.706	33°.5	32°.3	11°.94	11°.70	0°.24
"	3.157	45°.7	44°.5	14°.10	13°.89	0°.21
"	3.608	58°.(?)	—	—	—	—

The solution of concentration 3.157 changed from reddish brown at room temperature, to greenish yellow in the neighborhood of its freezing point. Salts separated out at about 58° for the solution which had the concentration 3.608 and, consequently, the freezing point lowering could not be determined.

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[1] Interpolated from the results of Jones and Bassett: THIS JOURNAL, **33**, 546 (1905).

Copper Bromide and Calcium Bromide.—(See Plates VII(*a*), XIX(*a*), XIX(*b*), XX(*a*) and XX(*b*); the first 3 are reduced to three-fourths of the original size). The concentrations of the mother solutions of copper bromide and of calcium bromide were, respectively, 2.186 and 4.236. The constant concentration of the copper salt in all of the solutions was 0.219. The concentrations of the calcium bromide were 0.000, 0.254, 0.508, 0.762, 1.017, 1.271, 1.525, 1.779, 2.033, 2.287, 2.542, 2.796, 3.050, 3.304, 3.588 and 3.807. All of the successive differences of concentration were equal to 0.2542, except the last one, which had the value 0.249.

The most pronounced colors of these solutions, in the order of increasing concentration of the dehydrating agent, were light blue, bluish green, green, yellowish green, brownish green and dull brown.

The spectrogram of Plate VII(*a*) will be discussed first. The negatives were taken on Cramer trichromatic plates. The photographic strip adjacent to the scales corresponds to the seventh solution of the series, *i. e.*, to the solution which had the concentration 1.525. The depth of the cell was 1.41 cm. Each exposure to light from the glower was 2.25 minutes in length. A spark exposure of 1.5 minutes was given for each one of the strips which pertained to the 3 most dilute solutions of the set. The negative strip for the solution which did not contain any calcium bromide, recorded the beginning of faint transmission at 0.373. The strip pertaining to the solution of concentration 1.107, showed that transmission began at 0.436 μ and continued to be weak to about 0.520 μ. Transmission was strong from 0.520 μ to the end of the negative.

The darkening of the next negative strip commenced exceedingly faintly at about 0.504 μ, and became very gradually more intense. The strip associated with the solution of concentration 1.525, showed extremely weak transmission from 0.664 μ to the end of the plate, the maximum being at 58; 5.

Plate XIX(a).

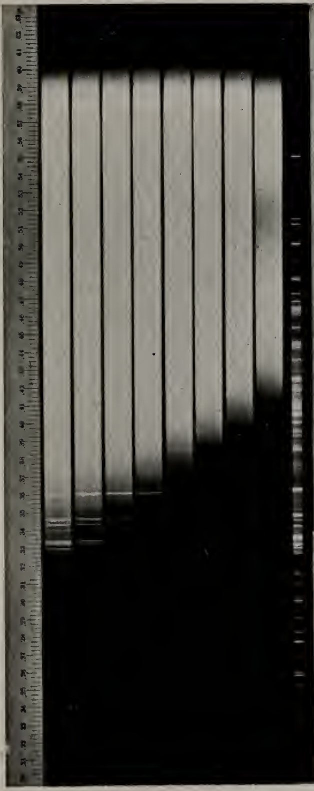
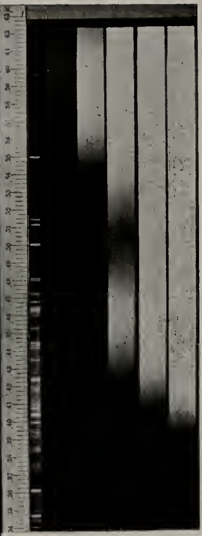


Plate XIX(b).



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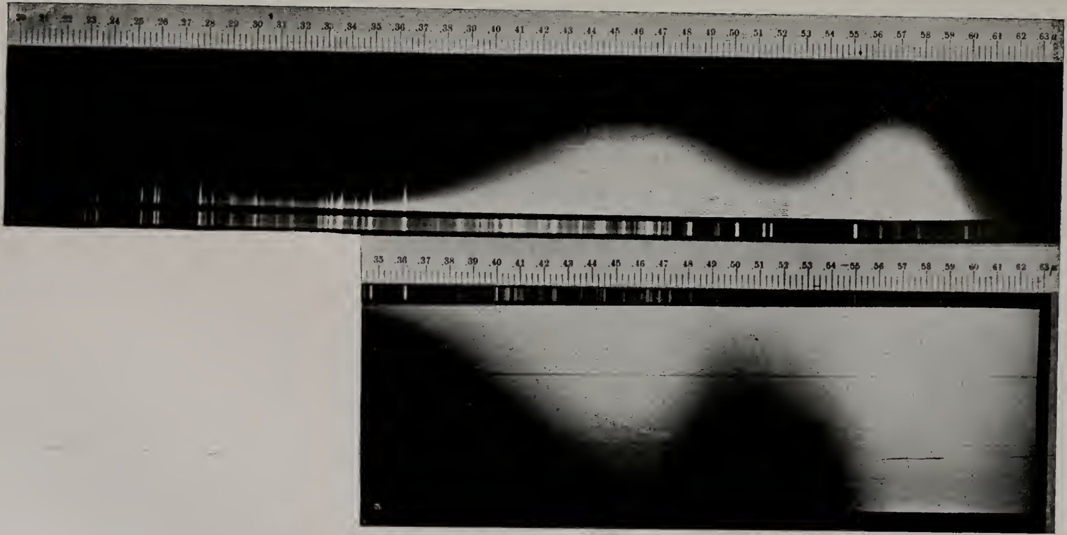
The facts presented by the negative of which Plate XIX(*a*) is a reproduction, will now be considered. The first 8 solutions of the complete series were photographed. The depth of the cell was 0.06 cm. and, therefore, the solutions, when in the cell, showed practically no color. The strips contiguous to the numbered scale and to the comparison spectrum correspond, respectively, to the solutions of concentration 0.000 and 1.779 of the dehydrating agent. The strip pertaining to the most dilute solution recorded the very faintest trace of the air line at 3007.0; the continuous background, however, ceased near 0.308 μ. The negative strip, corresponding to the eighth solution, showed that transmission began near 0.400. When due allowance is made for the known disturbing influences, the 8 strips of Plate XIX(*a*) seem to show that the end of the ultra-violet absorption band shifted in direct proportion to the increments of concentration of the calcium bromide.

It is now desirable to give the most salient points relative to Plate XIX(*b*). The negative of the spectrogram in question was made with a Cramer trichromatic plate. The seventh to the eleventh solutions, inclusive, had their spectra recorded by this plate. The strips pertaining to the solutions of concentration 1.525 and 2.542 are, respectively, nearest to the outside edge of Plate XIX(*b*) and to the scale. The depth of the cell was 0.06 cm. The duration of each exposure to the radiation of the filament was 2.25 minutes. Hence, the seventh and eighth solutions of the complete series have their absorption spectra given by both Plates XIX(*a*) and XIX(*b*). The negative strip, corresponding to solution of concentration 1.525, showed that transmission began at 0.383 μ. The third strip, counting from the outer edge of Plate XIX(*b*), recorded 0.417 μ for the beginning of transmission, and 0.500 μ for the middle of the region of rather weak transmission. The fourth strip showed very weak transmission from 0.436 μ to 0.484 μ, then apparent absorption from 0.484 μ to about 0.530 μ and, finally, stronger transmission from 0.530 μ to the end of the spectrogram. The negative strip pertaining to the solution of concentration 2.542 recorded very weak transmission from 0.555 μ to the end of the plate.

The most concentrated solution of the set was so opaque to light, that its absorption spectrum could only be satisfactorily recorded by the aid of the wedge-cell. For Plate XX(*a*) the angle of the liquid wedge was about 11′.7 and the depth of the absorbing layer increased linearally from zero to 0.11 mm. In the cell the solution appeared to be deep red. The absorption band in the blue-green could be distinctly seen with the aid of the eye-piece. The edges of this band are very diffuse and poorly defined. Obviously, the edge of the negative closest to the comparison spectrum was produced by the light that passed through the least depth of the solution, *i. e.*, nearest to the refractive edge of the liquid prism. Even for the thinnest layers the continuous background was completely absorbed from 0.200 μ to about 0.240 μ. The negative showed that the absorption began to decrease in the vicinity of 0.335 μ, and continued to do so according to a curve of gentle slope until it reached a minimum at 0.455 μ. From this point on, the absorption increased to a maximum near 0.517 μ, and then diminished again at the less refrangible side of the absorption band.

Except in so far as the wave length of the middle of the absorption band in the green is concerned, Plate XX(*b*), whose negative was taken with a Cramer trichromatic plate, fully confirms the facts as recorded by the spectrogram of Plate XX(*a*). The angle of the wedge was only 7′.8, and since the least depth was zero, the greatest depth of absorbing layer was about 0.08 cm. The 3 successive exposures to the light from the glower were each given 2.25 minutes. The negative was somewhat underdeveloped. It gave, for the first maximum of transmission, the wave length 0.454 μ. The maximum of absorption, but not the center of the band in the green, was recorded as 0.500 μ. The spectrogram of Plate XIX(*b*) gives a more correct graphical representation of the band in the blue-green than does that of Plate XIX(*a*). The asymmetry of this band, and its greater width of penumbra on the less refrangible side, was confirmed directly by observations.


.20 .21 .22 .23 .24 .25 .26 .27 .28 .29 .30 .31 .32 .33 .34 .35 .36 .37 .38 .39 .40 .41 .42 .43 .44 .45 .46 .47 .48 .49 .50 .51 .52 .53 .54 .55 .56 .57 .58 .59 .60 .61 .62 .63 μ
.35 .36 .37 .38 .39 .40 .41 .42 .43 .44 .45 .46 .47 .48 .49 .50 .51 .52 .53 .54 .55 .56 .57 .58 .59 .60 .61 .62 .63 μ

Plates XX(a) and XX(b).

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The results obtained by a rather extended series of eye observations, on the solutions which contained copper bromide and calcium bromide will now be given in some detail.

The solutions were first studied in pairs by the aid of the double compartment cell. The length of each absorbing column was, therefore, 2.5 cm. As the solutions became more and more concentrated, the band in the red gradually shifted its visible boundary to shorter wave lengths. The increments of absorption in the violet and blue appeared to become greater and greater as the more and more concentrated solutions were studied. The solution of concentration 1.107 of calcium bromide absorbed the blue-green and blue almost completely, and also dimmed the entire region of transmission appreciably more than the next less concentrated solution. In like manner, the solution of concentration 1.271, showed throughout weaker transmission than the next lower member of the series, and it absorbed completely all colors more refrangible than the green. In addition, this color was greatly weakened in intensity. The last 2 solutions just mentioned showed, at the more refrangible side of the green, a fairly long region of transmission, which was so extremely faint that the eye could not detect any color as such, but only an indefinite gray. The spectrum of the solution whose concentration was 0.254 was compared with that of distilled water. Very weak transmission of the same intensity began at 0.665 μ and 0.770 μ, respectively, for the solution and for the pure water. The solution also absorbed the extreme violet quite noticeably.

In order to study with the spectroscope the solutions of greater concentration that 1.525, as well as to obtain checks on the data secured photographically, the cell sketched in Fig. 3 was adjusted to a depth of 0.06 cm., and arranged so as to be used with its axis of figure horizontally. The following facts were then observed and noted: In this cell the solution of concentration 2.033 had a light yellowish brown color. The spectrum extended from about 0.747 μ to 0.425 μ. The weakening of transmission in blue-green was very delicate.

The spectrum transmitted by the solution of concentration 2.287 began about 0.740 μ, and continued to be uniformly bright to, say, 0.540 μ. At this wave length the penumbra of the absorption band in the blue-green commenced. The maximum of absorption appeared to have the position given by 0.500 μ. This absorption was not complete, since a little light could be seen at all points of the band, not excepting the maximum. Beyond this band transmission rose to a maximum near 0.465 μ, and then faded away to nothing in the vicinity of 0.435 μ. The numbers given for the extreme limits of transmission are, obviously, not very accurate, and are merely intended to suggest the positions of these boundaries. The spectrum of the next solution in order of concentration, 2.542, was, apparently, more complex than that of any other solution of the series. Transmission began at 0.737 μ, rose to a maximum at 0.652 μ and then increased in intensity to 0.603 μ. From this point to about 0.545 μ, the brightness of the spectrum seemed to remain constant, but much less bright than at the wave length 0.652 μ. A definite absorption band, whose middle was approximately at 0.508 μ, began near 0.545 μ. Beyond this band transmission rose to a maximum at 0.465 μ, and then gradually faded out to zero value in the neighborhood of 0.445 μ.

The transmission spectra of the solutions just discussed were comparatively bright, and extended over relatively wide regions of wave lengths, while the spectra to be described below were less intense and much prescribed. In other words, the transition was rather abrupt.

The solution of concentration 2.796 began to be transparent at 0.735 μ. The spectrum rose to a maximum of intensity near 0.657 μ, and then gradually fell off to small intensity at 0.600 μ. Transmission was pretty uniform between 0.600 μ and 0.550 μ. At the latter wave length the light decreased abruptly to zero. There was no visible return of transmission in the region of the shorter waves.

Transmission began at 0.730 μ, rose to a maximum at 0.660 μ, and decreased to almost no color near 0.590 μ, for the solution of concentration 3.050. An extremely weak region of transmission extended from a little beyond 0.590 μ to 0.575 μ. Because of its faintness, the subjective color throughout this region was gray.

The solution of concentration 3.304 transmitted chiefly bright red. The extreme limits of the spectrum were, approximately, 0.733 μ and 0.625 μ, the brightest spot being at 0.670 μ. Only red from about 0.730 μ to 0.640 μ was transmitted by the solution of concentration 3.558. Finally, the most concentrated solution of the series transmitted red from about 0.725 μ to 0.650 μ. The most intense portion of this spectrum was near 0.680 μ.

The lowerings of the freezing point of water produced by the solutions which contained copper bromide and calcium bromide are given below in Table XIV.

Table XIV.

1. Concentration of $CuBr_2$ in the mixture.	2. Concentration of $CaBr_2$ in the mixture.	3. Observed freezing point lowering of the mixture.	4. Lowering of freezing point if $CaBr_2$ alone were present.	5. Molecular lowering of freezing point if $CaBr_2$ alone were present.	6. Molecular lowering of freezing point for $CaBr_2$ in H_2O_1 alone.	7. Column 5 minus column 6.
0.219	0.000	1°.200	—	—	—	—
“	0.254	2°.836	1°.636	6°.44	5°.22	1°.22
“	0.508	4°.550	3°.350	6°.59	5°.58	1°.01
“	0.762	6°.696	5°.496	7°.21	5°.76	1°.45
“	1.017	9°.075	7°.875	7°.74	6°.40	1°.34
“	1.271	11°.90	10°.70	8°.42	7°.75	0°.67
“	1.525	15°.35	14°.15	9°.28	8°.71	0°.57
“	1.779	19°.5	18°.3	10°.29	9°.03	1°.26
“	2.033	24°.0	22°.8	11°.21	10°.42	0°.79
“	2.287	29°.5	28°.3	12°.37	11°.93	0°.44
“	2.542	36°.0	34°.8	13°.69	13°.31	0°.38
“	2.796	43°.5	42°.3	15°.13	14°.56	0°.57
“	3.050	52°.4	51°.2	16°.79	15°.80	0°.99
“	3.304	66°.5	65°.3	19°.76	17°.05	2°.71
“	3.558	?				

The solution of concentration 3.558 could not be frozen within the range of the scale of the thermometer, *i. e.*, between 0° and —80°.

[1] Interpolated from the results of Jones and Bassett: THIS JOURNAL, **33**, 550 (1905).

Copper Bromide and Aluminium Chloride.—(See Plates XXI(*a*) and XXI(*b*), both reduced to three-fourths of the original size.) The concentrations of the mother solutions of copper bromide and aluminium chloride were, respectively, 2.186 and 2.75. In the series of solutions discussed below, the constant concentration of the copper salt was 0.219. The concentrations of the dehydrating agent were 0.000, 0.275, 0.550, 0.825, 1.100, 1.375, 1.650, 1.925, 2.200 and 2.480. All the successive differences in concentration are equal to 0.275, except the last increment, which equals 0.280. As the amount of the dehydrating agent increased, the solutions changed from greenish blue to brown, passing through various intermediate shades of bluish green, green, olive and brownish green. The photographic strips corresponding, respectively, to the solutions which contained none of the aluminium chloride, and the greatest amount of this salt, are adjacent to the numbered scale and to the comparison spectrum. The depth of the cell was 1.41 cm. The most noticeable facts shown by the negative of Plate XXI. are the following:

The faintest trace of the intense cadmium doublet at 3612 was recorded by the strip corresponding to the aqueous solution which contained only copper bromide. The continuous background, however, faded out at about 0.371 μ. The spectrogram shows very clearly that for the first 7 or 8 solutions the absorption band, which included the entire ultraviolet region, advanced by ever-increasing increments as the concentration of the aluminium chloride became greater and greater. The seventh negative strip showed that transmission began at 0.502, and increased very gradually to about 0.527. From this point on, the solution was quite transparent. The strip corresponding to the most concentrated solution recorded relatively weak transmission of the less refrangible parts of the spectrum than 0.554 μ.

The negative, of which Plate XXI(*b*) is a reproduction, was taken with a Cramer trichromatic plate. The photographic strips correspond to the 5 more concentrated solutions of the complete set of 10. Obviously, the strip nearest to the scale pertains to the solution that contained the

Plate XXI(a).

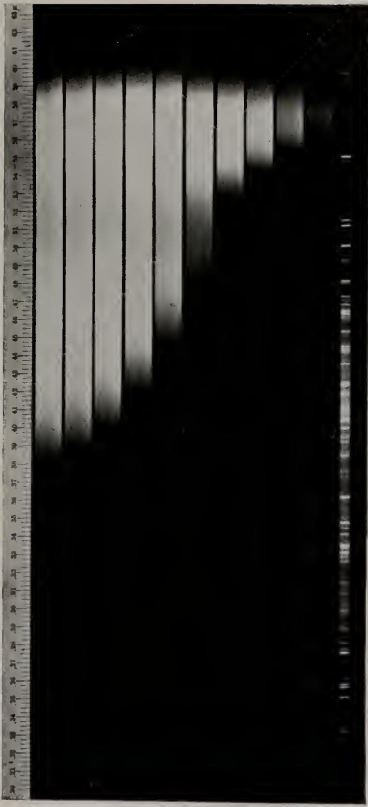
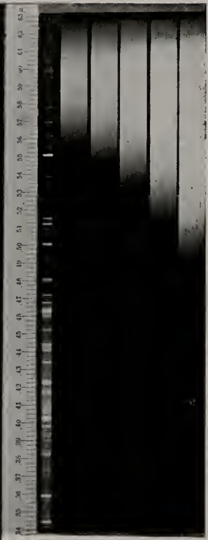


Plate XXI(b).



greatest amount of aluminium chloride. The depth of the cell was here also 1.41 cm. The time of exposure for the Nernst glower was 2 minutes. The strip corresponding to the solution of concentration 1.375, showed that transmission began weakly at 0.473 μ, approached gradually its full value, and continued complete nearly to the end of the plate. The photographic record began at about 0.552 μ for the strip pertaining to the most concentrated solution. The general outline suggested by the ends of photographic strips of Plate XXI(*b*), which ends show the beginning of transmission, curves in a direction exactly opposite to that of the contour outlined by the first 5 strips of Plate XXI(*a*). In other words, for the more concentrated solution in series, the successive increments of absorption decreased as the concentration of the aluminium chloride increased. By means of the two-compartment cell, eye observations were made on the solutions in pairs. The results obtained photographically were confirmed in all respects. One of the most important facts noted was that, as the concentration of the dehydrating agent increased in arithmetical progression, the successive increments of the absorption region which comprised the ultra-violet, first increased, and then subsequently decreased. Stated otherwise, the curve of absorption apparently possessed a point of inflection. The existence of the comparatively long region of weak transmission of the green for the sixth solution, was established visually as well as photographically. As far as the red end of the spectrum was concerned, every solution absorbed the red a little more than the next less concentrated member of the series. It was only possible to obtain a value for the mean displacement of the red or orange end of the spectrum. For the aqueous solution which contained only copper bromide, and for the most concentrated member of the set, transmission of about the same intensity began, respectively, at 0.670 μ and at 0.645 μ. Therefore, since there were 10 solutions in the series, the average displacement of the red end of the spectrum was 10 A. U.

The lowerings of the freezing point of water, produced by the solutions which contained copper bromide and aluminium chloride, are recorded below in Table XV.:

Table XV.

1. Concentration of $CuBr_2$ in the mixture.	2. Concentration of $AlCl_3$ in the mixture.	3. Observed freezing point lowering of the mixture.	4. Lowering of freezing point if $AlCl_3$ alone were present.	5. Molecular lowering of freezing point if $AlCl_3$ alone were present.	6. Molecular lowering of freezing point for $AlCl_3$ in H_2O alone.[1]	7. Column 5 minus column 6.
0.219	0.000	1°.200	—	—	—	—
"	0.275	3°.538	2°.338	8°.50	6°.05	2°.45
"	0.550	6°.900	5°.700	10°.36	7°.30	3°.06
"	0.825	11°.20	10°.00	12°.12	8°.79	3°.33
"	1.100	17°.1	15°.9	14°.45	10°.71	3°.74
"	1.375	25°.5	24°.3	17°.67	13°.06	4°.61
"	1.650	36°.0	34°.8	21°.09	15°.65	5°.44
"	1.925	51°.0	49°.8	25°.87	22°.07	3°.80
"	2.200	?				

The solution of concentration 1.925 changed from reddish brown to pea-green, as the temperature fell from room value to the neighborhood of —50°. On account of excessive undercooling it was not possible to freeze with a mixture of ethyl alcohol and solid carbon dioxide the solution of concentration 2.200. This solution became a light green, very viscous jelly at —75°.

GENERAL SUMMARY OF RESULTS.

Discussion of the Several Theories.—The theory of Engel, that the blue color of solutions of cobalt chloride is due to the presence of double salts, appears to us untenable for a number of reasons: In the first place, it has been shown by Jones and Ota[2] and Jones and Knight[3] that double chlorides, in general, even in very concentrated solutions, are largely broken down into the single salts, which are dissociated in the usual manner. In such solutions we should not have simply the molecules of the double salt, but a large number of the ions resulting from the dissociation of such a compound.

Again, this theory is entirely out of accord with the fact that a strong aqueous solution becomes blue when heated. The increase in the hydrolysis with the comparatively slight rise in temperature, is not sufficient to liberate enough hydrochloric acid to account for this color change on the basis of a compound being formed with this acid.

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[1] Interpolated from the results of Jones and Getman: Z. physik. Chem., **49**, 422 (1904).

[2] THIS JOURNAL, **22**, 5 (1899).

[3] *Ibid.*, **22**, 110 (1899).

Further, this theory is not in accord with the color changes which manifest themselves when water is added to solutions of cobalt chloride, etc., in methyl and ethyl alcohols and acetone, where no double salt can be present.

The following consideration would appear to have very direct bearing upon the theory under discussion: An examination of the spectrograms will show that, with increasing amount of the dehydrating agent or salt, the absorption bands widen. With increasing amounts of the dehydrating agents used in this work, more and more of the double halides, if they existed, would be formed, since the solutions would be more and more concentrated. This would mean that the vibrating, charged particle was becoming more and more complex. The above facts are not in harmony with one another. The most probable interpretation of the widening of the absorption bands with increase of concentration is, that the vibrating, charged particle is becoming of smaller and smaller mass, and can thus vibrate in resonance with a larger number of periods.

There are also a number of objections to the theory proposed by Ostwald to account for the color changes of cobalt chloride. It will be recalled that Ostwald takes the view that the blue color is due to the cobalt molecule, and the red color to the cobalt ion. This would not account for the great color change produced by warming a concentrated, aqueous solution of cobalt chloride. The dissociation would decrease a very small amount for the change in temperature from, say, 25° to 75° or 80°, as is shown by the work of Jones and West,[1] and especially by that of Noyes and Coolidge.[2] This slight change in the dissociation would be entirely incapable of accounting for the marked color changes produced. Further, the amount of hydrochloric acid liberated as the result of the increased hydrolysis with rise in temperature, would be far too small to drive back the dissociation sufficiently to produce such marked changes in color.

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[1] This Journal, **34**, 357 (1905).

[2] Z. physik. Chem., **46**, 323 (1903).

Another objection to this view is that the quantity of water required to color a blue alcoholic solution red, is altogether too small to produce a sufficient increase in the dissociation to cause the observed color change.

Further, the amount of water that is required to change very appreciably the color of a solution of cobalt chloride, rendered blue by the presence of aluminium chloride, is very small indeed, as is shown by Table VII. This small quantity of water could not, of course, materially increase the dissociation of the solution of cobalt chloride.

This shows that we cannot account for the color changes solely, or even chiefly, on the basis of dissociation.

That there are, apparently, insurmountable objections to the theory of Donnan and Bassett, that the blue color is due to complex ions of cobalt, is made evident by the following considerations:

The alcoholic solutions show, in general, the same color changes when water is added, as are manifested by the aqueous solutions in the presence of dehydrating agents. A comparison of the spectrograms in this paper, and the eye observations, with those in the paper immediately following this one, will show that the same absorption bands appear in the aqueous and in the non-aqueous solutions. These bands, however, undergo the well-known shift in position, due to a change in the dielectric constant of the medium produced by the presence of more and more of the dehydrating agent. It is, at least, very doubtful whether we should have the same ionic complexes in the non-aqueous solutions as in the solutions in water as the solvent.

Having pointed out the most serious defects in the various theories that have been proposed to account for such color changes as have been dealt with in this paper, we shall proceed to show how all the facts recorded in the preceding pages confirm the hydrate theory in the form emphasized by Jones.

Since the relation between the selective absorption of light and the existence of hydrates, may not be obvious, a brief discussion of this matter will now be given. Of course, in the present stage of our knowledge of the nature of solutions, it is not possible to form a detailed mechanical conception of the various processes which come into play in solutions, when arbitrary changes are made in concentration, in the temperature, in the solvent, etc. Nevertheless, the general view which we hold may be explained as follows: In the first place, *the phenomenon of absorption is, primarily, one of resonance,* and since light waves are electromagnetic waves, it follows that the absorbing system must be electrical in its nature. The *energy of a vibration of a given period will be absorbed to the greatest extent by a system whose natural period of vibration is most nearly equal to that of the first vibration,* and it may not be absorbed at all by a system whose period differs appreciably from that of the incident waves. In this way the selective phase of the phenomenon of absorption is explained. It is almost superfluous to state that the resonator, of which we are conceiving, may be very complex, and may have any finite number of discrete periods of vibration. Exactly how this resonator is related to the ion of electrolysis, as this term is usually understood, cannot be decided at present. Nor is this relationship a matter of fundamental importance to the question of the existence or non-existence of hydrates. It seems natural to suppose that the vibrations of this resonator would be strongly influenced by the nature of the medium surrounding it, not only by virtue of changes in the viscosity, specific inductive capacity, etc., of the medium, but also by the condensation around, or near it, of complexes of water molecules. The way in which these complexes or hydrates might affect the absorption of the resonator is as follows: The vibration of a given period of the resonator might be so greatly damped, either directly or indirectly, by the hydrate, that its amplitude would fall below the value which marks the limit of our experimental means of detecting absorption.

If this were the case we should not be aware of the existence of the absorption, and we should, therefore, say that no absorption of the given period takes place. In fact, when we say that pure water is transparent to light of one given period, for example, the D_3 line of helium, we do not mean that the absorption is absolutely zero, with mathematical exactness, but we do mean that it is, perhaps, indefinitely less than we can detect experimentally. Doubtless, if a column of absolutely pure water of sufficient length could be obtained, it would be found that the region of absorption for the Schumann waves would widen out simultaneously with the bands in the infra-red, until the entire visible spectrum would be dimmed by general absorption. The next question is, how should we expect the hydrates to affect the width of a given absorption band, or a limit of a region of absorption. The maximum of absorption of a band would correspond to that vibration of the resonator which was the least damped, and which, therefore, had the greatest amplitude; whereas the penumbra at the boundary of the band would correspond to those vibrations of the resonator which were damped to a great degree, and which, therefore, had very small amplitude. It has been tacitly assumed that the incident radiation was continuous, and practically comprised all of the periods of the resonating system. *If, now, the hydrate associated with a given resonator increased in mass by the addition of water, it would, of course, damp the vibrations more and more, and thus, by decreasing the amplitudes of the penumbral vibrations, cause the band to become narrower and narrower.* That absorption still existed in the region from which it had apparently disappeared, could be shown at once by simply increasing the length of absorbing column, until the penumbra had widened out to its original value, everything else being kept constant. *Conversely, when the extent of hydration decreases, the regions of absorption would widen out and extend over a greater range of periods and wave lengths.* Assuming that the argument advanced above is valid, then it does not seem possible to escape the conclusion that hydrates exist, since the theory accounts so perfectly for the facts. We shall deduce the evidence for this agreement in some detail from the spectrograms and other sources of information.

Plate II. shows that the regon of absorption in the ultra-violet widens out as the concentration of the cobalt chloride increases. The same fact is shown in Plates II and III(*a*), by the absorption band in the green. *As the concentration increases, the relative amount of water at the disposal of one cobalt system decreases, and, therefore, in accordance with the preceding theory, the band must become wider.*

The same phenomenon in the ultra-violet is shown by Plate V., for the solutions of copper chloride in water. Plate III(*b*) also brings out the facts for the band in the red.

It is obvious that in interpreting the spectrograms, the difference between the observed widening of the absorption bands, and the widening which would have theoretically been produced if a change in concentration had meant nothing more than an increase in the number of absorbing particles per unit volume, and not a change in their effective mass, had to be taken into account.

The well-known theoretical formula involving the laws of Beer and Lambert is $I = I_0 a^{dc}$, where d symbolizes the thickness of absorbing layer and c denotes the concentration. The remaining symbols have obvious definitions.

Further details concerning these laws may be found in the third volume of Kayser's "Handbuch der Spectroscopie," pp. 20, 25 and Chap. II. E.

Plates III(*c*) and VI. show conclusively the widening of the bands with increasing concentration, in the case of aqueous solutions of copper bromide. The data obtained from eye observations on the bands in the red confirm completely the spectrographic results.

Plates VIII., IX(*a*), IX(*b*) and XII. show that the bands in the ultra-violet and green widen out as the amount of calcium chloride in the aqueous solutions of cobalt chloride increases. It will be remembered that in these solutions the *mass of cobalt chloride was kept constant*, while the quantity of the dehydrating agent was varied. These facts agree perfectly with the theory, since the quantity of calcium chloride used has a much greater power to combine with water particles than the cobalt system has. Therefore, as the *concentration of* *the calcium chloride increases, more and more water is taken away from the cobalt chloride, so that the vibrations of the latter are less damped than before, and thus the absorption bands cover a wide range of period.*

The same phenomenon is shown by Plates XI(*a*) and XII. for the solutions containing variable amounts of aluminium chloride and a constant quantity of cobalt chloride.

The progress of the ultra-violet region of absorption, as the quantity of calcium chloride in the solutions containing a constant amount of copper chloride is increased, is very clearly shown by Plate XIII.

Plate XVII. brings out the same facts for the solutions having a constant mass of copper chloride and a variable quantity of aluminium chloride.

The absorption bands of solutions of copper bromide, which differ only in the amounts of calcium bromide contained in the solutions, extend over wider ranges of wave lengths as the percentage of the dehydrating agent increases. This is shown by Plates VII(*a*), XIX(*a*) and XIX(*b*).

The results of eye observations agree in detail with the facts derived from the photographic negatives. See especially Plates VIII(*a*), VIII(*b*), VIII(*c*) and VIII(*d*). When to solutions containing constant amounts of cobalt chloride, or of copper chloride, varying quantities of calcium bromide are added, the absorption phenomena are, in general, more complicated than in the cases just discussed, because of the effective formation, respectively, of cobalt bromide and of copper bromide. Similar conditions arise, of course, when either calcium chloride or aluminium chloride is added to solutions containing a constant amount of copper bromide. A careful study of the negatives corresponding to the mixed solutions of the kind just described, shows that the absorption bands of these solutions conform perfectly to the theory in question, and do not present any exceptions. Earlier investigations have shown that aluminium chloride is a stronger dehydrating agent than calcium chloride. This being the case, we should expect to find that a *given widening of an absorption band of a colored salt, so-called, which* *widening had been caused by the addition of a certain amount of calcium chloride, would be produced by a smaller amount of aluminium chloride.*

Consider the case of cobalt chloride with the other two chlorides just mentioned. See Plates IX(*b*), XI(*a*) and, especially, Plate XII. The pairs of solutions were made up so as to have the same colors when viewed in their bottles. The successive widths of the absorption band in the green, for the solutions which contained calcium chloride, are slightly, but only slightly wider than those of the band of the corresponding solutions of the aluminium chloride series. On the contrary, the concentrations of the calcium chloride were much greater than the concentrations of the aluminium chloride, everything else being kept constant. The concentrations are compared in Table XVI.:

Table XVI.

$CaCl_2$.	$AlCl_3$.
1.676	1.118
2.091	1.394
2.515	1.676
2.671	1.781
2.830	1.887
3.143	2.100
3.555	2.370

The region of absorption in the ultra-violet is not relevant, because of the intense absorption of the short waves by aluminium chloride alone.

Another illustration is afforded by the solutions of copper chloride, together with the chlorides of calcium and aluminium (see Plates XIII. and XVII.). A careful comparison of the negatives shows that the absorption produced by the most concentrated solution of aluminium chloride certainly extended farther into the visible spectrum than the corresponding band for the solution of calcium chloride, which was the third from the end of its series. The concentrations of the calcium and aluminium salts were, respectively, 3.518 and 2.482. The same fact may be brought out very sharply as follows: The two concentrations for the calcium chloride series, which come nearest to the concentration of the strongest aluminium chloride solution, and between which the latter concentration falls, are 2.435 and 2.706. The photographic strips pertaining to the calcium chloride solutions are the tenth and eleventh of Plate XIII., counting from the numbered scale towards the comparison spectrum. A single glance shows that both of these bands of transmission extend to much shorter wave lengths than the last strip of Plate XVII.

That it is, in general, much more difficult to remove the last molecules of water from a given compound than the first, is a well-known fact. Illustrations of this phenomenon are so numerous as to make it almost superfluous to cite specific instances. For all the cases examined, in which only one colored salt was present, and for all the absorption bands that had definite limits and were not accompanied by long regions of weak general absorption, it was found that, as the concentrations of the solutions increased in arithmetical progression, the increments of absorption at one side of the band gradually became less and less. This statement applies both to the solution which contained only one salt, and to those which contained a dehydrating agent together with a colored salt. Since a one-sided region of absorption in the ultra-violet may be looked upon, for the sake of convenience, as the less refrangible side of the band whose center lies beyond 0.200 μ, and hence out in the region of the Schumann waves, and since a one-sided region of absorption in the red is actually the more refrangible side of a band whose centre is situated in the infra-red, the preceding idea may be generalized by saying that the boundaries of all the absorption bands studied were concave towards their respective centers or maxima, as the case may be. The fact that the increments of absorption decreases as the concentration increases, means that the colored system resists the transfer of its associated water molecules to the dehydrating agent, more and more, as the actual number of its associated water molecules becomes less and less. From the standpoint of the colored salt, the process of making up solutions of the same volume, and at the same time increasing the concentration of the salt, is equivalent to taking away some of its molecules of water.

The bearing of this on the decreasing increments of absorption is obvious.

The cases where the spectrograms show that the boundary of the ultra-violet region of absorption was convex towards the shortest wave-lengths, are not really at variance with the preceding explanation, since this convexity is due to either of two causes, or both causes acting simultaneously. One of these conditions is as follows: For a given length of exposure, time of development, color of light, etc., there is an inferior limit of intensity of light, such that, if the intensity falls below this value, the sensitized film or plate will show no darkening even if overdeveloped. Now some of the solutions had very long, weak regions of general absorption at the edge of the ultra-violet region of complete absorption. Also, the intensity of this penumbral companion to the main band increased as the concentrations of the solutions of the series increased, at such a rate as to cause the photographic film to record, apparently, increments of absorption that were too large. In other words, for the more dilute solutions the plate would record the light which was only slightly weakened by the general absorption, as if there were no such absorption at all, and then for the more concentrated solutions it would not give any record of the faint light which passed through the penumbral region. The transition from one condition to the other might be either gradual or, apparently, sudden, according to obvious circumstances. Spurious results of this nature were sometimes corrected by the negative taken on the trichromatic plates, and they were always brought to light by the eye observations with the spectroscope.

The other cause for the apparently anomalous behavior of the contour of the ultra-violet region of absorption, is the gradual superposition of the bands belonging to the 2 colored salts. For example, when calcium chloride was added to the solution containing copper bromide, the absorption is complicated by the production in the solutions of calcium chloride and copper chloride. Of course, the compound absorption spectra of solutions of the kind just mentioned can be distorted by the peculiarities of photographic processes as well as the simpler cases. The well-known color changes which take place when fairly large variations are made in the temperature of the solutions, are in complete agreement with the present theory. For example, when a red solution of red cobalt is sufficiently warmed it becomes blue. As already explained, the blue and red colors correspond, respectively, to wide and narrow bands; or in terms of the theory, to small hydration and to relatively large hydration. But we know, from other lines of evidence, that the complexity of the hydrates decreases with rise in temperature, and thus we have another illustration of the wide applicability of the theory.

When a solution of cobalt chloride has been made deep blue, at room temperature, by the addition of some one of the strong dehydrating agents, it turns red when cooled to the neighborhood of its freezing point. The explanation of this phenomenon, in terms of the theory, is obvious. The corresponding color changes for the copper salts can be explained in exactly the same manner as has been done for cobalt chloride.

Before concluding the discussion of the interpretation of the spectroscopic data, it is desirable to emphasize the fact that all the color changes investigated take place very gradually and continuously, and that there are no sudden variations in the bands and regions of absorption. Perhaps the most striking color change of all is that from blue to green, manifested by copper chloride. The one solution is blue because there is no absorption band in the violet, and yet there is a strong band in the red. The other solution is green because a band has pushed its end out of the ultra-violet into the visible spectrum, and absorbed the violet and, perhaps, weakened the blue.

The band in the red has likewise encroached on the visible spectrum. The apparently abrupt change from blue to green is only due to the fact that the visible spectrum is limited by the sensitivity of the retina to a certain region of wave lengths. If we could see distinctly into the ultra-violet as far as 0.200 μ, we should probably be less hasty in writing about mixtures of the colors of certain ions and molecules. What is meant by the color of an ion? How do absorption bands mix colors?

In conclusion, it is appropriate to call attention to certain facts which were brought out by the present investigation, and which have no direct bearing on the theory of hydrates.

Tables I. and III., for the freezing point lowerings of cobalt chloride, together with either calcium chloride or calcium bromide, show that these solutions change with time. The nature of the change is such as to increase the molecular lowering of the freezing point; in other words, the solutions undergo hydrolysis.

Table VII. shows that the volume of water necessary to change a color of the series in question approximately to that of the next more dilute solution of the set, decreases as the concentration of the first solution increases. The solutions contain cobalt chloride and aluminium chloride.

The reason for the decrease just noted is as follows: When the solutions are very concentrated they contain a relatively small amount of water and, therefore, it requires the addition of only a very small quantity of the latter to change the color of the solution to that of the next lower number of the series. When, on the other hand, the solutions contain a larger amount of water to begin with, it requires a greater quantity than formerly to bring about a definite color change. In other words, the question is one which concerns the ratio of the amount of water added, to the quantity already present, and it does not relate, primarily, to the absolute volume of water concerned. A careful study of the 5 curves for electrical conductivity, shows that the viscosity is chiefly responsible for the decrease in conductivity with increase in the concentration of the dehydrating agent, after a maximum of a curve has been reached. Stated in a slightly different way, the decrease in the velocity of the ions is so much greater than the simultaneous increase in the number of ions, that the conductivity decreases with increase in concentration. The fact that the maxima of the curves for the solutions which contained the same dehydrating agent, occur at approximately the same concentration of this agent, quite independent of the nature of the colored salt in the solution, is due to the relatively small number of ions of the colored salt, as compared with the number of ions of the dehydrating agent. Moreover, as would be expected, the greater the viscosity of the dehydrating agent, the lower the concentration corresponding to the maximum of the curve. Compare, in this connection, the calcium chloride solutions with those of aluminium chloride.

Finally, we wish to express our thanks to the Physical Department for placing at our disposal the conditions necessary for carrying out this work.

PHYSICAL CHEMICAL LABORATORY,
JOHNS HOPKINS UNIVERSITY,
May, 1906.

THE ABSORPTION SPECTRA OF CERTAIN SALTS IN NON-AQUEOUS SOLVENTS, AS AFFECTED BY THE ADDITION OF WATER.

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[This investigation was carried out with the aid of a Grant from the Carnegie Institution.]

Apparatus.

The spectrograph, spectroscope, photographic materials, etc., used in the study of non-aqueous solutions were the same as those employed in the earlier investigation[1] of the absorption spectra of aqueous solutions. Since, however, the various parts of all the cells used for aqueous solutions were fastened together with cement, which is soluble in alcohol and acetone, it became necessary to design a cell which would not be so acted upon by the solutions to be investigated. Moreover, since no strongly adhesive cement could be found which would satisfy the requirements of being insoluble in water, alcohol, acetone, etc., it was decided to construct a cell of entirely new design, which would be absolutely free from cement of any kind.

[1] THIS JOURNAL, **37**, 126 (1907).

A vertical section of the cell, enlarged to twice the natural size, is shown by Plate I., and the details of the several parts may be explained as follows: In its fundamental principles, the cell consisted of 3 distinct parts: (*a*) an outer glass tube with a quartz bottom to hold the liquid; (*b*) an inner glass tube with a quartz plate at the lower end, to regulate the depth of the liquid, and to cause the upper surface of the absorbing layer of solution to be both plane and parallel to the quartz bottom of the larger glass tube; (*c*) a mechanism which would act as a stopper to the system of glass and quartz just mentioned, and which would also enable the experimenter to adjust the cell for any desired depth of absorbing layer from zero to the full capacity of the cell, *i. e.*, about 3.5 cm.

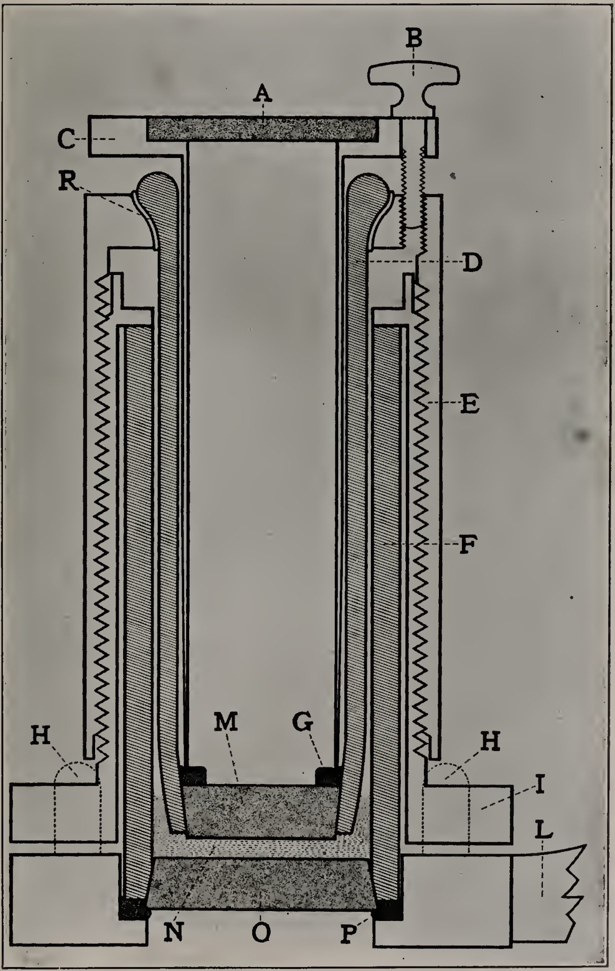
The separate parts of this piece of apparatus will be described in the order in which they would be assembled for actual use. M denotes a plane parallel plate of quartz, ground carefully in the form of a frustum of a cone, so as to fit very accurately into the conical hole at the lower end of the glass tube D. The thickness of this quartz plate was 4.6 mm., and its least diameter was 12.6 mm. The glass tube was blown with a thick shoulder at its upper end. The plate M was first slipped into place in the tube D, and then the rubber washer G was pushed down against the quartz by introducing the brass tube C into the glass tube. In order to prevent dust from entering the inner tubes, the plane parallel quartz plate A was permanently set into a cylindrical depression in the upper end of the glass tube C. This plate was 2 mm. thick and 20 mm. in diameter.

The brass tube widened out into a sort of plate at its upper end, and this projection was pierced by 3 holes at the vertices of an equilateral triangle. Through these holes suitable screws passed, and one of these is shown at B of Plate I. After the brass tube C had been introduced into the glass tube, the washer R, made of blotting paper, was slipped up over the outside of the glass tube until it would not pass through the shoulder of this tube. Then the group of parts thus far described was let down through the hole at the upper end of the hollow brass cylinder E, as far as it could go, *i. e.*, until the washer R was tightly squeezed between the glass and brass surfaces. The 3 screws were next pushed through their respective holes, and turned until the quartz plate M was forced, liquid-tight, into the conical hole in the glass tube, care being taken at the same time to so adjust the system as to have the axis of rotation of the glass tube and quartz plate parallel to the axis of the brass cylinder E. A thread of convenient pitch had been accurately cut in the inner surface of this cylinder. The purpose of this thread, as well as that of a fine line or groove which had been turned on the outside of the cylinder, in a plane at right angles to the axis of the latter, will be explained below.

Whenever the cell had been entirely taken apart, which was not often necessary, the distance between the plane of the lower surface of the quartz plate M, and the plane of the lower end of the cylinder E, had to be measured and recorded, since this distance varied with the thickness of the two washers and with the pressure exerted by the screws. The number expressing this distance was one of several numbers that had to be known in order to adjust the cell for a given depth.

The thread at E was next fitted to the thread that had been accurately cut to fit it on the outside of the brass cylinder I. Then the two cylinders were screwed together until the distance between the fine cut around the outside of E, and a certain point of the upper plane surface of the flange at the bottom of the cylinder I, had the proper value. This distance was, of course, measured along a generating line of the outer surface at E and, therefore, perpendicular to the plane just located. The assemblage of parts explained above formed a complete system in itself, and comprised all of parts L and C, using the notation of the remarks introductory to the more detailed discussion of the cell. The flange at the bottom of I was provided with 3 large and 2 small holes, and all of them pierced it parallel to the axis of the cylinder. The larger holes fitted closely over 3 pillars, H and H, while the smaller ones corresponded to 2 little

Plate I.



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screws. The pillars and screws were not in the plane of the diagram. The object of the pillars and screws will be explained a little later. The cylinder I was also turned so as to have a collar on its interior near the top.

When the desired depth of absorbing liquid had been determined upon, the basis of intensity of color, etc., the distance between the line around E and the upper plane of the flange of I was found by the addition of 3 numbers. One of these was a constant of the apparatus, 1.34 cm., and the other 2 expressed, respectively, the required depth of solution, and the distance from the lower plane surface of the quartz plates M to the plane of the lower end of the brass cylinder E. As an example from practice, for a depth of 2 cm. the sum was 1.34 + 2.00 + 0.69 = 4.03 cm., *i. e.*, the 2 cylinders E and I had to be screwed around each other until the line to the flange was equal to 4.03 cm.

Conversely, knowing this distance as well as the 2 cell data, it was merely a matter of algebraic addition to obtain the effective depth of the cell.

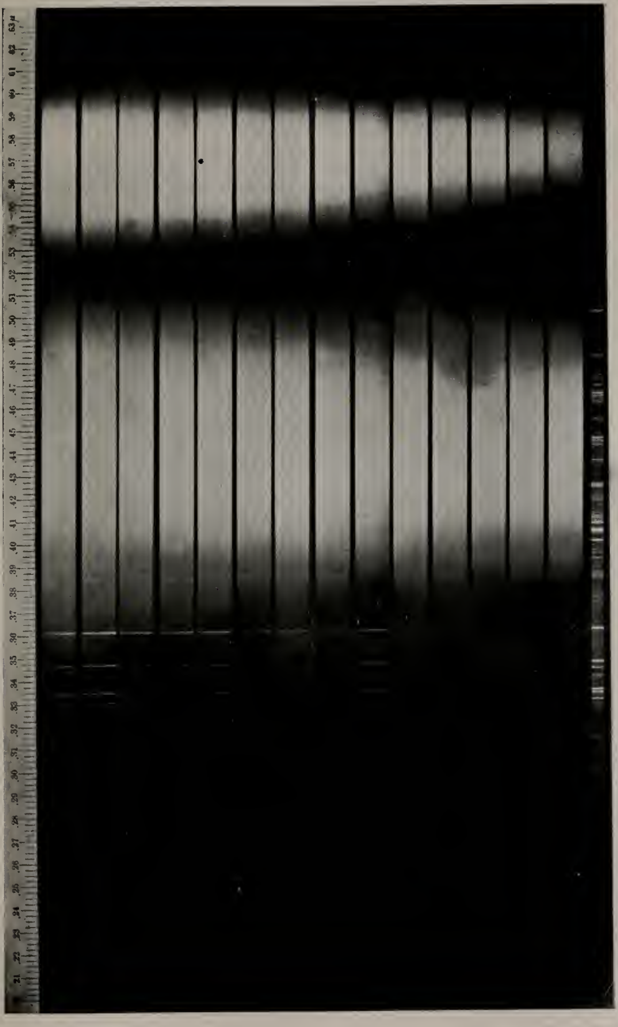
The remaining parts of the apparatus had the characteristics described below, and were assembled as follows: L denotes the handle of a stout, hollow, cylindrical plate, which formed the bottom of the complete cell. The interior of this plate was turned out so as to leave a flange at the bottom upon which the rubber washer P was placed. The 3 pillars mentioned above projected vertically from, and were rigidly attached to the plate L. Two holes had been tapped out of this plate to correspond accurately to the smooth holes of the flange of I. After laying the washer P on the flange of L, and after pushing and turning the quartz plate M tight up into the conical holes of the glass tube F, the transparent system was set vertically with its lower end resting symmetrically on the washer. The thickness and the smallest diameter of this quartz plate were, respectively, 4.6 mm. and 19 mm. The solution to be studied, N, was next poured into the vessel constituted by F and O. It was necessary to measure the depth of the liquid, and it was found convenient to make this depth 2 mm. greater than the effective depth of the cell.

The assembled system of parts A, B, C, D, G, I, M, R was next let down over the glass tube F, until the upper flange inside the cylinder I rested on top of this tube. The 3 pillars H, guided the system into the correct position, and prevented any rotation of the cylinders I and L around each other. Lastly, the 2 little screws were passed through the holes in the lower rim of I, and the 2 cylinders were screwed tightly together. This operation completed the adjustment of the cell. It is seen at once, from the preceding explanation, that the liquid or solution in question came only in contact with glass and quartz surfaces, while the vapor touched both glass and brass walls. Since the vapors of the solutions studied did not act on brass, glass and quartz, and since the apparatus did not leak, the cell gave entire satisfaction. For vapors which would attack brass, but not the silicates, it is easy to see how a system could be designed which would differ from the one just described in having coaxial glass tubes dip into a trap of some neutral liquid, instead of the brass cylinders E and I. Moreover, it would be quite possible to design the parts of the cell in such a way as to impart to the liquid the shape of a wedge or prism of adjustable angle and depth.

Solutions.

The solutions were made up as follows: A chosen volume of pure water was run out of a burette into a measuring flask. Then some of the mother solution of one of the colored salts was poured into the flask, and thoroughly mixed with the water until the volume of the resulting homogeneous solution was exactly equal to the calibrated capacity of the flask. In the following account of the work, the amount of water in a given solution will be expressed in per cent of the total volume of the solution. For example, if 5 cc. of water were made up to 200 cc. of solution, the amount of water would be given as 2.5 per cent, or simply 2.5. The colored salts used were: Cobalt chloride, copper chloride and copper bromide. The solvents employed were: Methyl alcohol, ethyl alcohol and acetone. Special precautions were taken to have both the colored salts and the solvents as free from water as possible.

Plate II.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Cobalt Chloride in Methyl Alcohol.—(See Plate II., which is reduced to seven-eighths of the original size.) The concentration of the mother solution was 0.993. The percentages of water in the solutions were 12.00, 9.50, 7.00, 6.00, 5.00, 4.00, 3.50, 3.00, 2.00, 1.50, 1.26, 1.01, 0.50, 0.000. The successive differences in per cent were 2.50, 2.50, 1.00, 1.00, 1.00, 0.50, 0.50, 1.00, 0.50, 0.24, 0.25, 0.51, 0.50. As the quantity of water increased, the color of the solution gradually changed from the purple of the mother solution to a pale pink, passing through the intermediate tints. Photographic strips, corresponding to the solutions which contained the greatest and least amount of water, are adjacent, respectively, to the numbered scale and to the comparison or spark spectrum. The depth of cell was 2.0 cm.

The spectrogram shows a region of absorption in the ultraviolet and violet, and a band in the green. The air line at 3007 A. U., was very faintly recorded by the strip corresponding to the solution which contained the greatest amount of water, but the continuous background did not extend beyond about 0.314 μ. The middle of the band in the green was 0.517 μ. As shown by the corresponding strip, transmission began near 0.373 μ, for the mother solution of cobalt chloride in the methyl alcohol. The middle of the band in the green was at 0.525 μ. Therefore, one effect of the addition of water is to shift this band towards the blue. It is interesting to note, in this connection, that the center of the absorption band in the green was displaced towards the red by about 100 A. U., when the solvent was changed from water alone[1] to methyl alcohol. This absorption band widened very gradually as the amount of water in the successive solutions decreased. In fact, for the mother solution the negative strip indicated that transmission began near 0.505 μ and 0.540 μ at the sides of this absorption band. The band was very weak for the solution which contained the greatest amount of water. It must, however, be remembered that the other solution was not quite 0.1 N, cobalt chloride being only slightly soluble in methyl alcohol.

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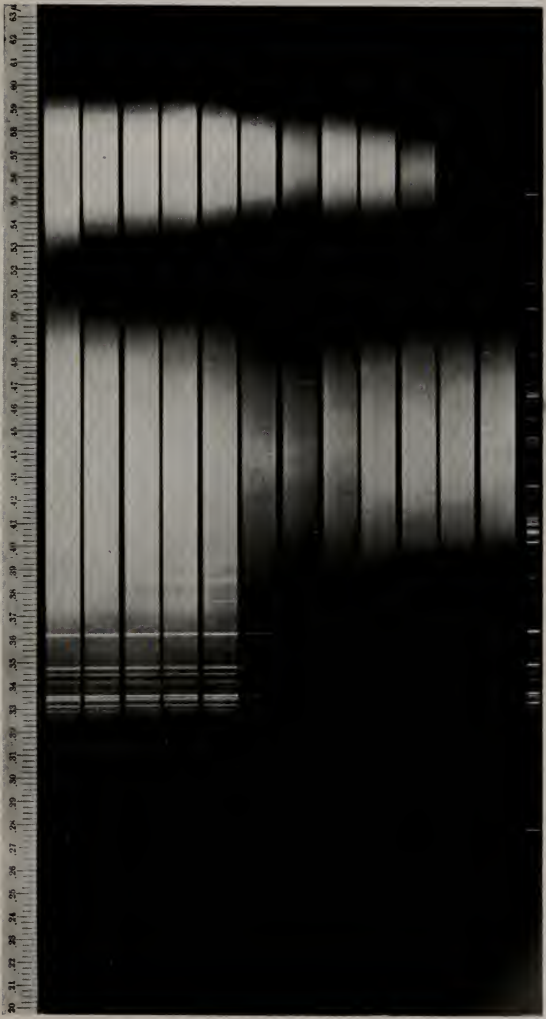
[1] THIS JOURNAL, 37, 162 (1907).

Eye observations of typical solutions of the set gave the following results: The depth of cell used was 3.0 cm. The mother solution had a clear purple color, with a decided reddish tinge, when viewed by diffuse daylight transmitted through the cell. Transmission began about 0.766 μ, and extended to the beginning of the absorption band in the green. Weak, partial absorption appeared in the red at 0.704 μ. The brightest region of transmission was in the immediate neighborhood of 0.625 μ, *i. e.*, in the yellow. No narrow absorption bands in the red, orange or yellow, such as were observed for aqueous solutions of cobalt chloride, were visible. The band in the green was narrow but intense, its maximum being near 0.540 μ. It was much more abrupt on the less than on the more refrangible side. For one definite exposure, a photographic film does not necessarily show the position of the maximum of intensity of an asymmetric absorption band, so that it is not surprising to find 0.525 μ for the center of the photographic band, and 0.540 μ, for the maximum of absorption with the prism spectroscope. To see if there are any other absorption bands, the cell was filled to the brim of the larger glass tube, and the rest of the system was not put in place. In this manner a column of solution 4.5 cm. long was obtained. The several faint maxima and minima of transmission could be seen in the red. If the solution could have been made more concentrated, or better, if the cell had been deeper, it is extremely probable that all the bands observed in aqueous solutions could have been seen with the alcoholic solution in question. As the spectra of the solutions which contained greater and greater amounts of water were brought into the field of view, it was observed that the various regions of absorption grew weaker and weaker, and that the entire spectra remained qualitatively similar to the spectrum of the mother solution. Of course, the regions of weak absorption around 0.704 μ soon disappeared. The maximum of intensity of the absorption band in the green had the wave length 0.525 μ, for the solution which contained the greatest percentage of water, (12.00). Consequently, the maximum of this band was displaced about 150 A. U. towards the blue, when

Plate III.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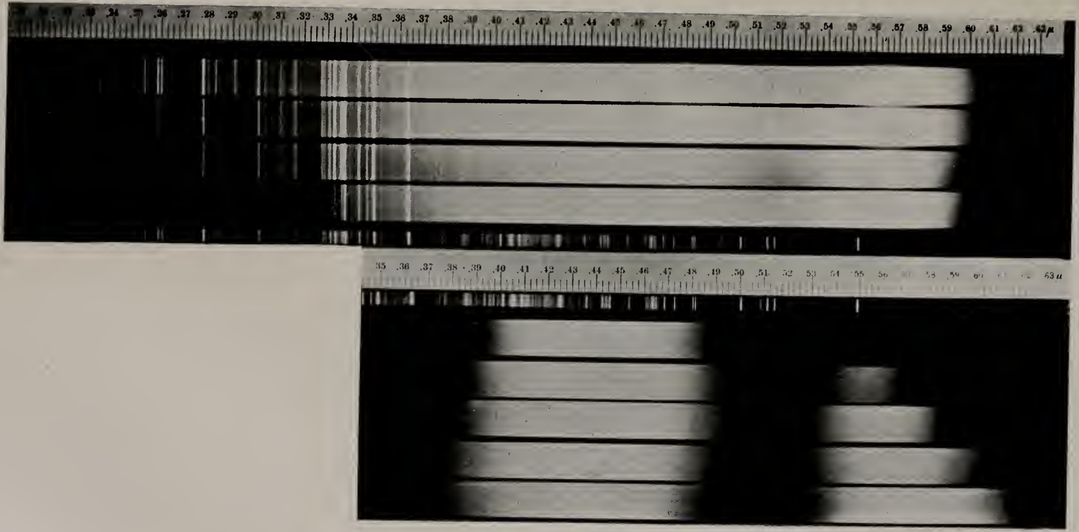
the amount of water in the solution was changed from 0.000 to 12.00.

Cobalt Chloride and Ethyl Alcohol. — (See Plates III and IV(*b*).) The concentration of the mother solution of cobalt chloride in ethyl alcohol was 0.0967. The percentages of water in the solution were 20.0, 10.0, 8.0, 7.5, 7.0, 6.0, 5.5, 5.0, 4.0, 3.0, 2.0 and 0.0. The successive differences in per cent were 10.0, 2.0 0.5, 0.5, 1.0, 0.5, 0.5, 1.0, 1.0, 1.0, 2.0. As the quantity of water decreased, the colors of the solutions changed from pink, through various shades of violet, to deep blue. The photographic strips corresponding to the solutions which contained the greatest and least amounts of water, are contiguous, respectively, to the numbered scale and to the comparison spectrum of Plate III. This spectrogram will be discussed before Plate IV(*b*). The depth of the cell was 2.00 cm; but as this number is given from memory, it may not be exact. As would be expected, the same general regions and bands of absorption were possessed by the solutions of cobalt chloride in ethyl alcohol and water, as by those in which methyl alcohol took the place of ethyl alcohol. The negative strip pertaining to the solution which contained the greatest amount of water, barely recorded the intense zinc line of wave length 2502.1 A. U. The continuous background ceased about 0.280 μ. The middle of the band in the green as shown by the negative was near 0.516 μ. For the solution whose percentage of water was 2.0, the negative strip gave 0.519 μ as the middle of the band in the green. Hence, the photographic band was displaced towards the blue by about 30 A. U., as the percentage of water was increased from 2.0 to 20.0. The strip corresponding to the mother solution showed transmission between the extreme limits 0.384 μ and 0.508 μ. The last 3 strips, and especially the very last one, showed the existence of appreciable general absorption in the yellow and orange. The negative for Plate IV(*b*) was taken with a Cramer trichromatic plate. The solutions used were the last 5 of the set of 12, in other words, the 5 which contained the smallest amounts of water. The strip pertaining to the mother solution is closest to the scale. The depth of the cell was 2.00 cm. The exposure for the Nernst filament lasted for 2 minutes. The negative recorded the middle of the absorption band in the green as at 0.510 μ, for the solution which contained 5.00 per cent of water. The 5 strips show distinctly the gradual shift of the middle of this band towards the red, as the quantity of water in the solutions decreased from 5.00 to 0.00 per cent. They also exhibit the progress of absorption both in the violet and in the orange and yellow. In fact, the strip pertaining to the mother solution shows no transmission of the yellow. The middle of the region of transmission between the band in the violet and the band in the green, moved towards the red, whereas the center of the bright region between the band in the green and the band in the orange shifted towards the blue, as the percentage of water decreased.

The results obtained by eye observations with the Hilger spectroscope were as follows: The depth of cell used was 2 cm. With only air in the path of the beam of light, the spectrum began near 0.776 μ. The mother solution transmitted faintly a band of red from 0.775 μ to 0.735 μ. The more refrangible limit was quite well defined. An intense region of absorption extended from 0.735 μ to 0.575 μ. Transmission began again in the blue-green. This color, however, was weak. Absolutely no light of shorter wave length than 0.417 μ could be seen, which shows that the ultra-violet region of absorption extended into the visible spectrum by at least 170 A. U.

The solution which contained 2 per cent of water transmitted a band of red, like the mother solution. Then the absorption was complete as far as 0.629 μ. Faint transmission began at 0.269 μ and passed over into rather strong transmission in the vicinity of 0.597 μ. In other words, a single broad band possessed by the mother solution had broken up into 2 bands, of which the more refrangible was much less intense and well defined than its companion in the red. A relatively weak spot in the transmission appeared near 0.52 μ.

The solution which contained 3 per cent of water had a complicated spectrum, very much like the spectra belonging to aqueous solutions of cobalt chloride to which a comparatively large quantity of calcium chloride, of calcium bromide,



Plates IV(a) and IV(b).

or of aluminium bromide had been added. The maximum of transmission in the red was near 0.734 μ, and the adjoining region of intense absorption had its maximum at about 0.690 μ. Then a series of bands of incomplete opacity and transparency succeeded one another. The position of the maxima of absorption were recorded as 0.636 μ, 0.615 μ, 0.600 μ, with the brightest transmission at 0.627 μ; 0.608 μ marked the center of a very faint maximum of transmission. The next region of relatively strong transmission extended from 0.596 μ to about 0.535 μ. The band in the general neighborhood of 0.52 μ was weak and very diffuse at its limits.

For the solution containing 4 per cent of water there were maxima of transmission at 0.730 μ and 0.627 μ. The maxima of the absorption band had the wave lengths 0.695 μ, 0.636 μ, 0.615 μ and 0.600 μ. The stronger band at 0.695 μ transmitted a little light even at its maximum. The bands at 0.615 μ and 0.600 μ were very faint. The band in the green was too diffuse and indefinite to have the position of its center or even of its maximum determined. For the 5.5 per cent solution the bands at 0.636 μ, 0.615 μ, 0.600 μ had become so extremely faint that they could only be seen by moving the spectrum across the field of view of the telescope. All the remaining bands were much weaker.

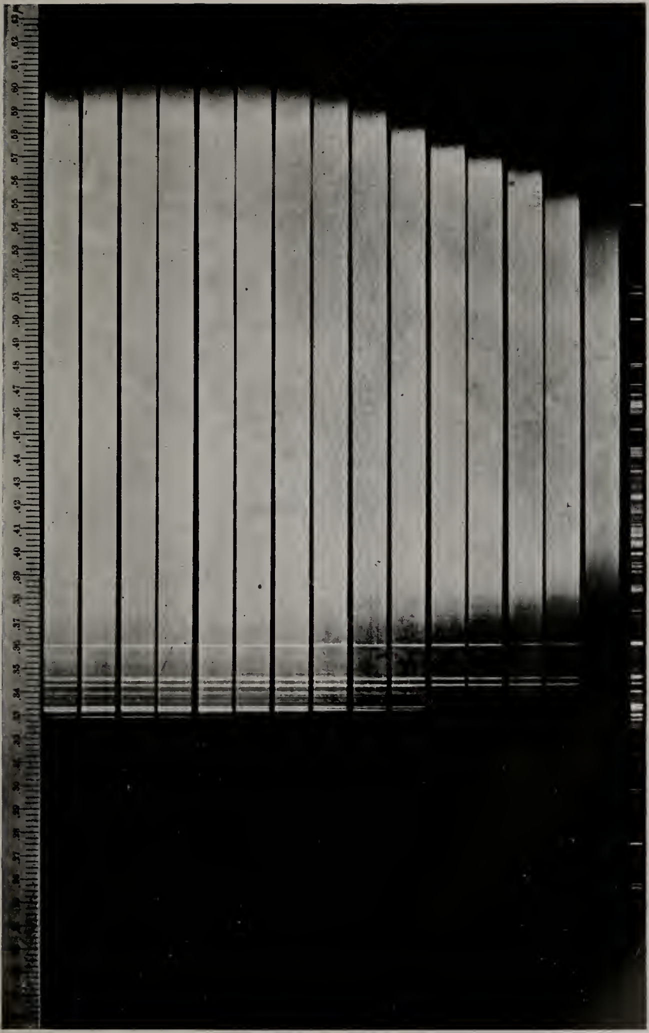
For the 7 per cent solution the band in the red had become very weak, while for the 8 per cent solution it had become a mere shadow and lost its identity as a band.

A solution which contained 40 per cent of water exerted very slight absorption in the extreme red, and very weak diffuse absorption in the blue-green.

Cobalt Chloride in Acetone.—(See Plate V., which is reduced to seven-eighths of its original size.) The concentration of the mother solution of cobalt chloride in acetone was 0.0154. The percentages of water in the solutions were 28, 26, 24, 22, 20, 18, 16, 14, 12, 10, 8, 6, 4, 2, and 0. Each successive difference in this sequence equals 2. When placed in the cell, at a depth of 2 cm., the solutions whose percentages of water varied from 28 to 16, inclusive of the latter number, were delicate pink. Beginning with the solutions having 14 per cent of water, the color changed to blue, which was at first very faint and then gradually increased as the amount of water decreased. The mother solution had a very deep blue color. The photograph strips adjacent to the numbered scale and to the comparison spectrum correspond, respectively, to the solutions that contained the greatest amount of water and no water at all. The spectrogram shows the existence of a region of very intense absorption in the ultra-violet, and another region in the orange. No band appeared photographically in the green. The negative strip for the 28 per cent solution showed that the ultra-violet region of absorption ended abruptly at 3250. That this limit of absorption did not vary rapidly as the amount of water decreased, is shown by the fact that the strip for the 2 per cent solution gave the wave length of complete absorption as 3329. In other words, this limit only moved by about 80 A. U., while the percentage of water changed from 28 to 2. In addition to the abrupt limit of absorption, the existence of ever increasing weak absorption of the extreme violet and least refrangible ultra-violet, is shown by the last 5 or 6 strips, which correspond to the solutions that contained smaller amounts of water. For the mother solution this general absorption was relatively strong. Although the strip for the mother solution recorded very faintly the air line at 3331.5, nevertheless, the continuous background only began to grow strong near, say, 0.375 μ. The last 8 or 9 negative strips showed distinctly the existence of absorption in the orange and yellow. Also the more refrangible limit of this band did not shift in direct proportion to the percentage of water in the successive solutions. The strip for the mother solutions shows that transmission of sufficient intensity to affect the photographic film stopped at about 0.554 μ.

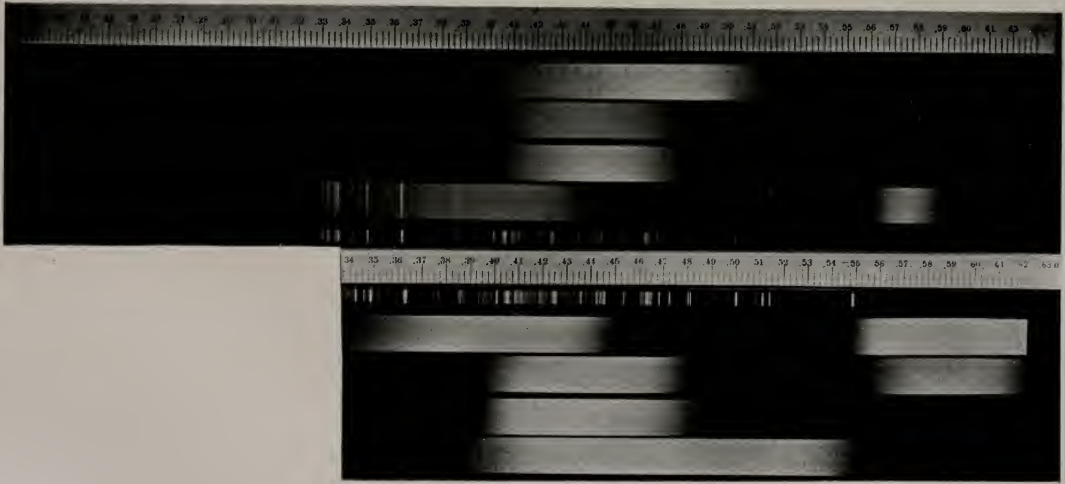
The spectroscopic study of the bands in the red and orange brought out the following facts: The cell depth was 2.00 cm. For the mother solution transmission began near 0.570 μ and increased to about 0.554 μ. The green and blue regions are not very bright, and the nearest approach to transparency seemed to be in the indigo. Visible transmission ceased at

Plate V.



0.424. The spectrum of the 4 per cent solution was qualitatively like that of the mother solution. The wave lengths which corresponded to 0.570 μ, 0.554 μ and 0.424 μ for the mother solution were, respectively, 0.599 μ, 0.574 μ and 0.416 μ, in the case of the 4 per cent solution. The solution which contained 6 per cent of water was the first to show definite absorption bands. It transmitted very faintly the red from 0.77 μ to 0.731 μ. One absorption band extended from 0.731 μ to 0.630 μ, and another from 0.616 μ to about 0.596 μ. Slight transmission separated these 2 bands of complete absorption. The complete spectrum for the 8 per cent solution was more complicated than that of the 6 per cent solution. The red was faintly transmitted from 0.77 μ to 0.721 μ, with the maximum of brightness near 0.741 μ. Complete absorption from 0.721 μ to 0.651 μ was followed by very weak transmission between 0.651 μ and 0.634 μ. A strip of relatively weak transmission which, however, was much more intense than its less refrangible neighbor, began at 0.634 μ and had its middle at 6255 A. U. This was followed by 2 comparatively narrow, symmetrical bands of almost complete absorption, whose maxima had the wave lengths 0.613 μ and 0.6005 μ. The middle of the intervening and very faint band of transmission was at 0.607 μ. The spectrum for the 10 per cent solution was very much like that of the 8 per cent, the absorption bands, of course, being somewhat weaker. For the 12 per cent solutions the bands were very faint indeed. The strongest band had the approximate wave length 0.700 μ. The narrow bands at 0.613 μ and 0.6005 μ, could only be seen by moving the spectrum across the field of view. The 14 per cent solution showed only one absorption band. This band was in the extreme red and was very weak. The 16 per cent solution had no visible bands, as such. The transmission from the bluish color of 14 per cent, to the pinkish tinge of the 16 per cent solution, was due to the gradual disappearance of the absorption bands in the red, and not to an abrupt or continuous change of any kind whatsoever. The solutions having more than 16 per cent of water showed no absorption bands in the spectroscope.

Before taking up the discussion of the copper salts, it is desirable to compare the spectra of the mother solutions of cobalt chloride with one another, and to consider how much of the ultra-violet absorption was due to the solvents themselves. See Plates VI(*a*) and VI(*b*). Consider first the negative for VI(*a*). The concentrations of the cobalt chloride in acetone, in ethyl alcohol, in methyl alcohol and water, were, respectively, 0.010, 0.097, 0.099 and 0.325; this last solution, diluted from the original mother solution, was used in the preceding study of aqueous solutions. The first solution, which was not the mother solution for Plate V., was blue, with a slight greenish tinge. The second solution was blue with a slight reddish tinge. The second solution was deeper blue than the first, due largely to the difference in concentration. The third and fourth solutions were, respectively, purple and red. The photographic strips nearest to the numbered scale and to the comparison spectrum correspond, respectively, to the solutions in acetone and in water. The 4 strips are in the same order as that in which the solutions are named above. The depth of the cell was 2.048 cm. The strip pertaining to the acetone solution recorded very faintly the intense doublet at 3330, but the extreme limits of the continuous background were 0.370 μ and 0.550 μ. The strip corresponding to the ethyl alcohol solution gave the extreme limits of transmission as 0.388 μ and 0.496 μ. The negative strip pertaining to the methyl alcohol solution gave the limits of one region of transmission as 0.385 μ and 0.495 μ. Faint transmission was recorded from 0.555 μ, towards the red. An absorption band extending from 0.495 μ to 0.555 μ. The density of the negative was greater in the region of the blue and violet for the solution in methyl alcohol than for the one in ethyl alcohol. Also the maxima of transmission as given by the negative for the solutions in acetone and in methyl alcohol were, respectively, near 0.470 μ and 0.442 μ. The strip for the aqueous solution showed the trace of a line at 2502.1, but the continuous background faded away near 0.288 μ. The band of absorption in the green comprised the region from 0.452 μ to 0.551 μ.



Plates VI(a) and VI(b).

The contrasts of the regions of absorption and of transmission of the 4 solutions under consideration, are very distinctly shown by Plate VI(*b*). The negative for this spectrogram was taken with a Cramer trichromatic plate. The solutions were the same as for Plate VI(*a*), and their spectra were photographed in the same order. The strip corresponding to the aqueous solution is adjacent to the scales. The depth of the cell was 2 cm., and the length of exposure for the glower was 2 minutes. The extreme limits of transmission for the solution of acetone were 0.370 μ and 0.562 μ. The corresponding limits for the solutions in methyl alcohol were about 0.385 μ and 0.497 μ. The strips pertaining to the last 2 solutions showed no return to transparency in the yellow and orange. The solution in methyl alcohol transmitted light from about 0.390 μ to 0.500 μ. This was followed by an absorption band from 0.500 μ to 0.547 μ. The aqueous solution had a band of complete absorption from about 0.462 μ to 0.543 μ. The region of transmission in the yellow and yellow-orange, was much more intense for the aqueous solution than for the one in methyl alcohol. The shifts experienced by the centers of the regions of absorption and transmission, when the solvents were changed, due allowance being made for the several concentrations, were large, and are rather strikingly shown by Plate VI(*b*). The results of eye observations on the spectra of the 4 solutions in question, have already been given, so that nothing more than a brief résumé of the facts is necessary. The solution in acetone transmitted a faint band of red, the middle of which was near 0.761 μ. The solution in methyl alcohol transmitted more strongly a region of red from about 0.775 μ to 0.735 μ. The spectrogram of Plate VI(*b*) gives the photographic positions of the less refrangible limit of the absorption band in the green. The solution in methyl alcohol showed a weak absorption band near 0.704 μ, while the aqueous solution was too dilute to give the bands in the red. Therefore, that region of absorption which may be called, for brevity, the band in the green, moved its center to shorter and shorter wave lengths, as the solvents successively used were acetone, ethyl alcohol, methyl alcohol and water.

Plate IV(*a*) gives the ultra-violet absorption of the 4 solvents used. The strip adjacent to the numbered scale corresponds to distilled water, and the next strip belongs to methyl alcohol. The strip nearest to the comparison spectrum corresponds to acetone. The remaining strip resulted from light transmitted by ethyl alcohol. The depth of the cell was 1.41 cm. As is well known, water is exceptionally transparent to short light waves, so that the negative strip for this liquid recorded as many lines in the remote ultra-violet as was shown by the comparison spectrum. The shortest wave length given by the strip for methyl alcohol was 2313.0. The strong cadmium line, however, was just barely visible on the negative. The intense lines at 2558.0, 2573.1 and 2712.6 were rather fully transmitted. The continuous background for waves more refrangible than 2748.7 was extremely weak. The third strip showed that ethyl alcohol was more transparent than methyl alcohol to the remote ultra-violet, since it recorded distinctly the lines at 2265.1, 2288.1, 2313.0 and 2321.2. On the other hand, the lines at 2558.0, 2573.1 and 2721.6 were not quite as strong after passing through the ethyl alcohol as they were after emerging from the methyl alcohol. Taking the continuous background into account, as well as the spark lines, the negative shows that methyl alcohol has a one-sided region of absorption in the ultra-violet, whereas ethyl alcohol has a region of semitransparency in the neighborhood of 0.230 μ, with strong absorption on both sides. For all ultra-violet and visible waves less refrangible than 2748.7 the transmission of these 2 alcohols seems to be identical. Acetone showed intense selective absorption in the ultra-violet, because the associated photographic strip recorded nothing beyond 3282.4. This line was very much weakened, and the correct limit of this region of absorption was 3302.7. The conclusion is that the ultra-violet absorption of the cobalt chloride was only masked by that of the solvent in the case of acetone. In all of the other examples studied, the ultra-violet absorption was due largely to the cobalt chloride in the solution, and not so much to the solvents as such.

Plate VII.

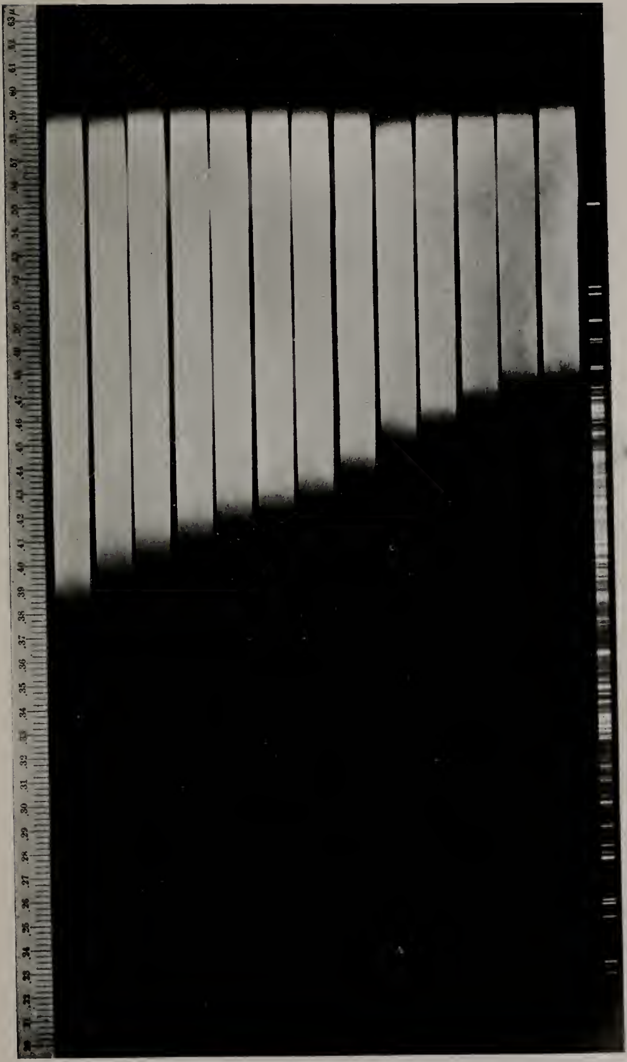

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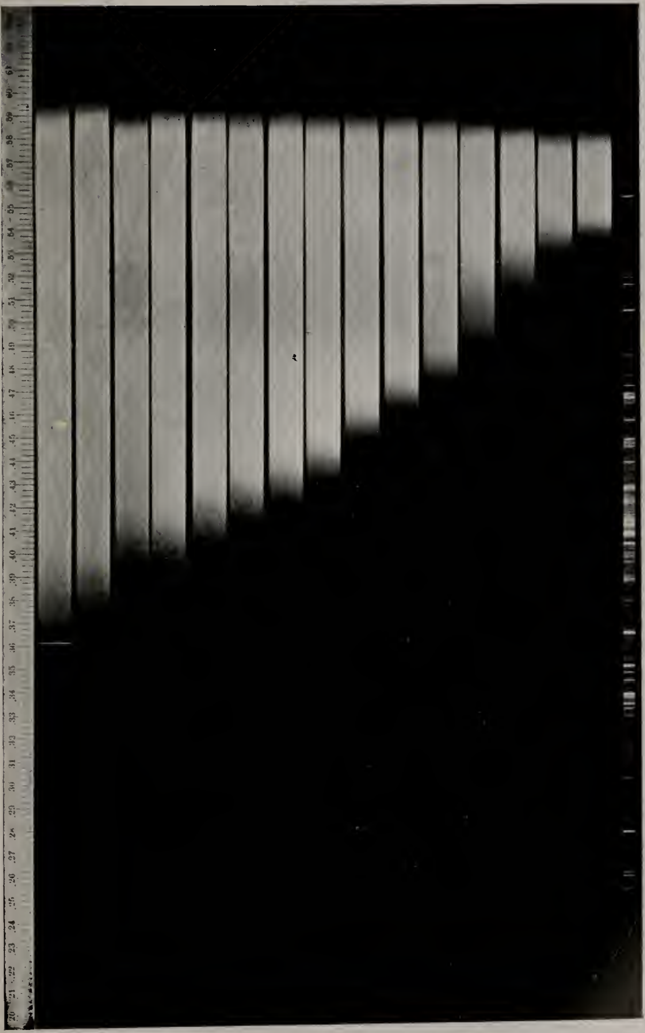
Plate VIII.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Copper Chloride in Methyl Alcohol.—(See Plate VII.) The concentration of the mother solution of copper chloride was 0.283. The percentages of water in the solutions of the series were: 40, 36, 32, 28, 26, 24, 22, 20, 16, 12, 8, 4, and 0. All the successive differences in this sequence of numbers were equal to 4 per cent, except the fourth, fifth, sixth and seventh. Each of the 4 exceptional increments was equal to 2 per cent. To obtain a general idea of the dependence upon the amount of water present of the limit of absorption of the band, which included the ultra-violet, it is convenient to omit the fifth and seventh photographic strips from consideration. As the amount of water decreased, the color of the solutions varied from greenish-blue, through pure green, to a green with a yellow tint.

The strip corresponding to the 40 per cent solution is adjacent to the numbered scale, and that belonging to the mother solution lies next to the comparison spectrum. The depth of the cell was 2.40 cm. The negative showed only 1 region of absorption, and it included the entire ultra-violet, the negative strips corresponding, respectively, to the solution which contained the greatest amount of water, and to the one which was anhydrous, gave the very beginnings of transmission as 0.375 μ and 0.480 μ. The complete spectrogram shows that the increments of absorption decreased gradually as the percentage of water decreased in arithmetical progression.

The spectroscope revealed the existence of a one-sided region of absorption in the red. The depth of cell used was 2 cm. The limit of visible transmission moved towards the infra-red, as the quantity of water in the solutions increased. The approximate wave lengths of this limit were 0.65 μ and 0.67 μ, respectively, for the mother solution and for the solution which contained 40 per cent of water.

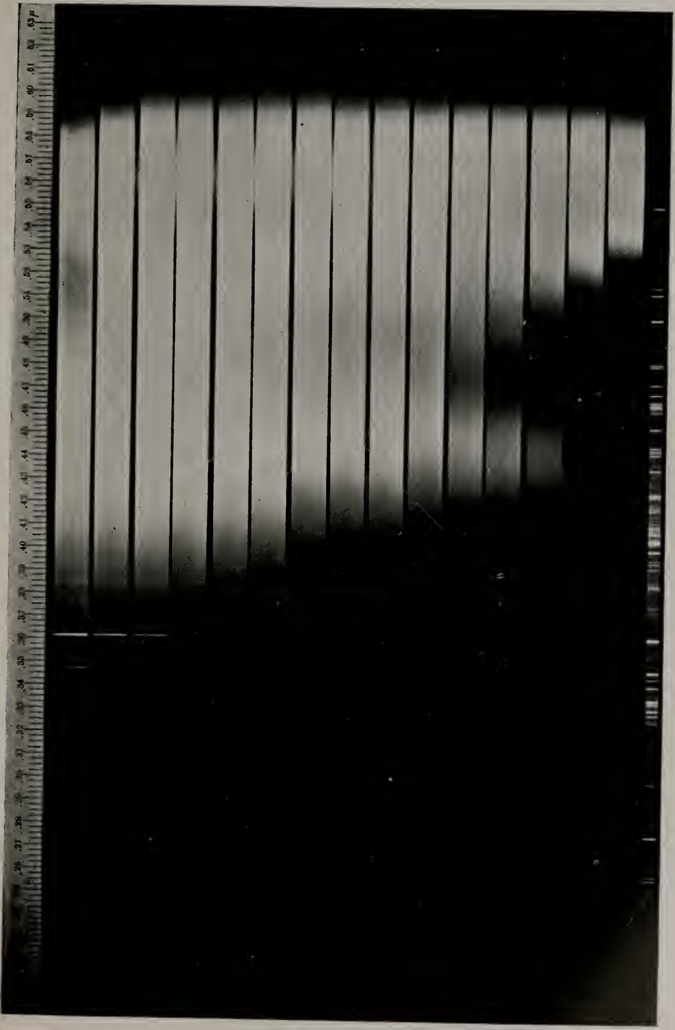
Copper Chloride in Ethyl Alcohol.—(See Plate VIII., which is reduced to seven-eighths of the original size.) The concentration of the mother solution of copper chloride was 0.321. The percentages of water in the solutions of the complete set were 56, 52, 48, 44, 40, 36, 32, 28, 24, 20, 16, 12, 8, 4 and

0. Each successive difference equals 4 per cent. The colors of the liquids, when viewed in the cell, varied from blue, through greenish blue, bluish green, green, and yellowish green to olive, as the percentage of water decreased from 56 to 0. The photographic strip contiguous to the numbered scale belongs to the solution which contained 56 per cent of water. The next strip corresponds to the 52 per cent solution, etc., until, finally, the strip adjacent to the comparison spectrum corresponds to the anhydrous mother solution. The depth of the cell was 2 cm. The spectrogram shows a one-sided region of strong absorption in the ultra-violet and violet, and suggests another like region in the yellow and orange. The negative strip corresponding to the solution which contained the greatest amount of water, recorded faintly the strong cadmium doublet at 3467, but the continuous background faded out at near 0.350 μ. Transmission began weakly at 0.520 μ for the mother solution. The curve outlined by the ends of the photographic strips, appeared to be convex toward the ultra-violet region of absorption, throughout the greater part of its course; whereas, in general, the curves obtained for copper chloride, whether in water alone or in water which also contains some dehydrating agent, were concave towards the left.

The spectroscope showed that there was an absorption band in the infra-red, which extended into the visible spectrum. For the anhydrous mother solution transmission began at about 0.635 μ, and for the solution which contained the greatest amount of water, it commenced at 0.700 μ. Eye observations on the spectra of the solutions in question showed that the limit of absorption in the red receded to longer wave lengths as the percentage of water in the solution increased.

Copper Chloride in Acetone.—(See Plate IX. which is reduced to seven-eighths of the original size.) The concentration of the mother solution of copper chloride in acetone was 0.022. The percentages of water in the various solutions of the set were 28, 24, 22, 20, 18, 16, 12, 10, 8, 6, 4, 3, 2, 1 and 0. The first and sixth differences were 4 per cent. The last 4 increments reached 1 per cent, and all the remaining increments

Plate IX.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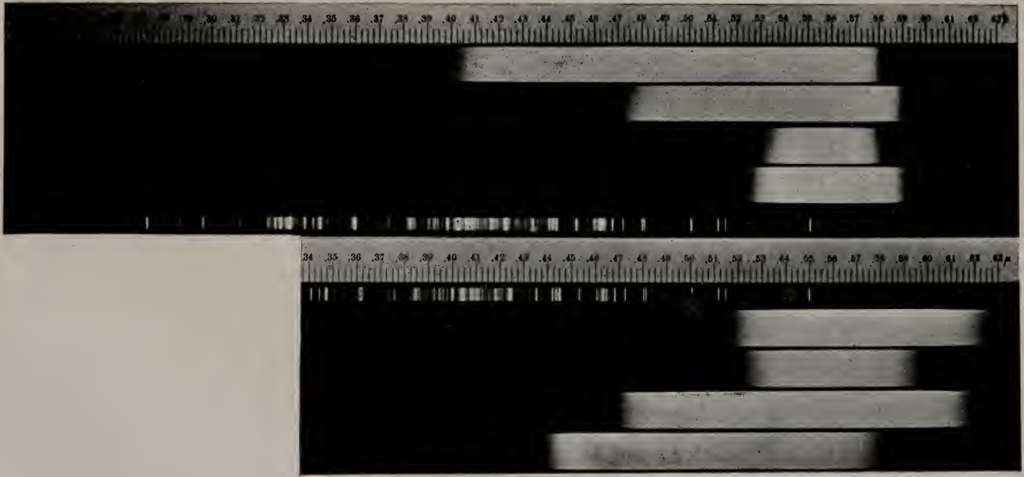
2 per cent. The solutions varied in color from bluish green to dark olive, as the percentage of water decreased from 28 to 0. The strip most remote from the numbered scale corresponds to the anhydrous mother solutions, the next strip pertaining to the solution which contained 11 per cent of water, etc., until the strip adjacent to the scale corresponds to the solution which contained the greatest amount of water. The depth of the cell was 2 cm. The complete spectrogram shows a region of strong absorption in the ultra-violet and violet, and also a band in the blue-green. The negative strip pertaining to the solution which contained 28 per cent of water recorded faintly the zinc doublet at 3345, but the continuous background practically ceased at 0.344 μ. The locus of the limits of the region of absorption, which comprises the entire ultra-violet, is a smooth curve concave towards this region. The strip corresponding to the 4 per cent solution barely indicated the existence of an absorption band whose center was at 0.473 μ. The remaining strips, which correspond to the solutions that contain less than 4 per cent of water, show that the band both widened out rapidly, and had its center displaced slightly towards the red, as the amount of water decreased. In fact, a strip pertaining to the anhydrous solution showed that the band in the blue-green had united with the wide region of absorption in the ultra-violet, so that no light of wave length shorter than 527 μ was transmitted. The middle of the transparent region between the two bands of absorption in question was at about 0.436 μ.

Eye observations with the spectroscope, and with the cell 2 cm. deep, brought out the following facts: The mother solution transmitted, freely, orange, yellow and yellow-green. Its spectrum began at 0.706 μ and ended near 0.507 μ. Because the spectrum began at 0.775 μ, when the cell was not in the path of the light incident upon the slit of the spectroscope, it is evident that the mother solution absorbed all the deep red. The 2 per cent solution began to transmit at 0.727 μ. The transmission spectrum began to be much weakened near 0.503 μ, and showed a weak band of partial absorption at the more refrangible side of the wave length. Faint light could be distinguished as far as 0.435 μ. The minimum of transmission in the blue-green could also be observed in the case of the 4 per cent solution. The solution which contained the greatest amount of water began to transmit at about 0.750 μ. The entire series of observations showed that the more refrangible limit of the band which absorbed the red, receded towards the infra-red as the percentage of water in the solution increased.

For the sake of comparison, the spectra of the solutions of copper chloride in the 4 pure solvents were recorded side by side, photographically. See Plates X(*a*) and X(*b*). The concentrations of the solutions in water, in methyl alcohol, in ethyl alcohol and acetone as solvents were, respectively, 0.795, 0.283, 0.321, 0.022. The depth of cell used was 1.50 cm. for both plates. In the cell the aqueous solution was blue, the solution in methyl alcohol was yellowish green, the solution in ethyl alcohol was very dark green and the solution in acetone was brownish yellow. The negative strips corresponding, respectively, to the solutions in water and in acetone, are adjacent to the numbered scale and to the comparison spectrum. The strip nearest to the one that pertains to the aqueous solution, corresponds to the solution in methyl alcohol. The negative of Plate X(*a*) showed that the extreme limits of transmission for the aqueous solution were 0.397 μ and 0.598 μ. Only the more refrangible limit of the region of visible transmission could be recorded by the Seed film, for the solution in methyl alcohol. This limit was given as 0.472 μ. The limits of faint transmission for the solution in ethyl alcohol, were recorded as 0.523 μ and 0.598 μ. The negative strip corresponding to the solution in acetone as solvent, showed that transmission began at about 0.519 μ, and extended beyond the region of sensibility of the photographic emulsion.

The negative for Plate X(*b*) was taken with a Cramer trichromatic plate. The concentrations of the non-aqueous solutions were the same as for Plate X(*a*). The concentration of the aqueous solution of copper chloride was 1.590, *i. e.*, twice as great as formerly. The solution was green with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Plates X(a) and X(b).

a bluish tinge. The length of the exposure for the Nernst glower was 2 minutes. The photographic strips succeed one another in exactly the same order for Plate XI(*b*) and for Plate XI(*a*). However, the strip corresponding to the solution in acetone is adjacent to both scales, while the one pertaining to the aqueous solution is nearest to Plate X(*a*). The extreme limits of transmission were shown by the negative to be 0.431 μ and 0.591 μ for the aqueous solution. The strip corresponding to the solution in methyl alcohol showed that transmission began near 0.462 μ, and only became weakened to a very slight extent at the extreme end of the plate. The strip pertaining to the solution in ethyl alcohol gave the limits of transmission as 0.512 μ and 0.618 μ. The acetone solution began to transmit at about 0.507 μ, and continued to do so beyond the field of view of the spectrograph. The results of eye observations, combined with the data obtained photographically, show that as the solvent for copper chloride was successively water, ethyl alcohol, methyl alcohol and acetone, the middle of the region of transmission in the visible spectrum moved to longer and longer wave lengths.

Copper Bromide in Methyl Alcohol. — (See Plates XI., which is reduced to three-fourths of the original size, and XII(*a*).) The concentration of the mother solution of copper bromide in methyl alcohol was 0.122. Instead of being made up in the usual way, the solutions were prepared by measuring the volume of the mother solution, and then adding water to the mark on the measuring flask, the percentages of water in the solutions of the series being 52, 44, 40, 36, 32, 28, 24, 20, 18, 16, 14, 12, 10, 8, 4 and 0. Therefore, the successive differences in percentage were 8, 4, 4, 4, 4, 4, 4, 2, 2, 2, 2, 2, 2, 4, and 4. In the cell, which was at a depth of 0.76 cm., the first 4 solutions were practically colorless, the next 3 were of an extremely pale, greenish yellow color, the succeeding 6 were greenish yellow, the third from the last was brownish yellow and the last 2 were dull brown. For the spectrogram of Plate XI. the strips corresponding, respectively, to the solution which contained the greatest amount of water, and to the anhydrous solution, are adjacent to the numbered scale and to the comparison spectrum. The negative strip corresponding to the 52 per cent solution, recorded faintly the zinc line at 3262.4, but the continuous background hardly extended as far as 0.334 μ. The strip pertaining to the 8 per cent solution, showed that weak general absorption had set in beyond the limit of the intense ultra-violet region of absorption. In other words, transmission began at about 0.453 μ, and continued to be relatively weak as far as 0.527 μ. Of course, the maxima and minima of photographic sensibility exaggerated the phenomenon in question. The strip corresponding to the 4 per cent solution showed very faint transmission from 0.482 μ to about 0.530 μ.

The strip pertaining to the mother solution recorded extremely faint transmission from 0.543 μ towards the red. The last 3 strips showed the existence of general absorption in the orange. Due allowance being made for the values of successive differences in the amounts of water in the solutions, as well as for variations in photographic sensibility, the complete spectrogram shows that the curve for the limit of ultra-violet absorption was convex towards the region of shortest waves, at least throughout the greater part of its course. The negative for Plate XII(*a*) was taken with a Cramer trichromatic plate. It gave the spectra of the 5 solutions of the set in question, which contained the smallest percentages of water, including no water at all. The cell depth was, as above, 0.76 cm. Each exposure to the light from the glower was 2 minutes. The negative strip, corresponding to the 8 per cent solution, showed that transmission began at about 0.453 μ, and remained relatively weak as far as 0.503 μ. The strip pertaining to the solution which contained 4 per cent of water, gave 0.498 μ as the wave length of the very beginning of faint transmission. The strip belonging to the anhydrous mother solution showed an extremely faint transmission from about 0.530 μ to the end of the spectrogram.

Eye observations with the spectroscope confirmed qualitatively the above results, and also brought out some additional facts relative to the red region in the spectrum. For

Plate XI.

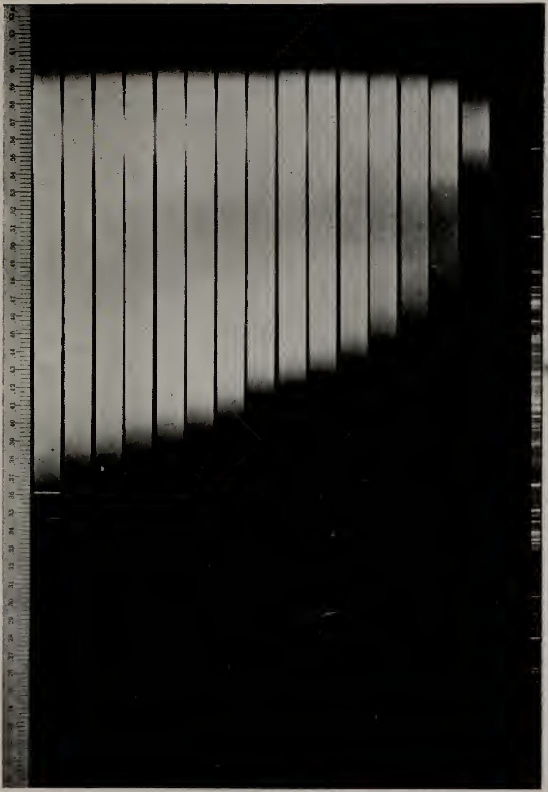
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Plate XII(a).

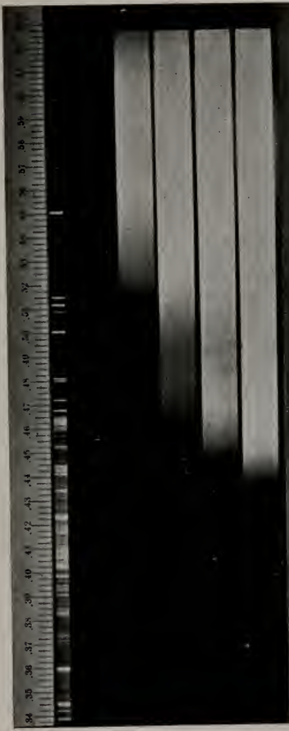
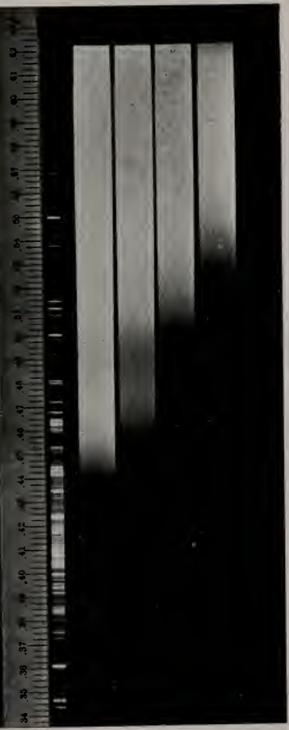


Plate XII(b).



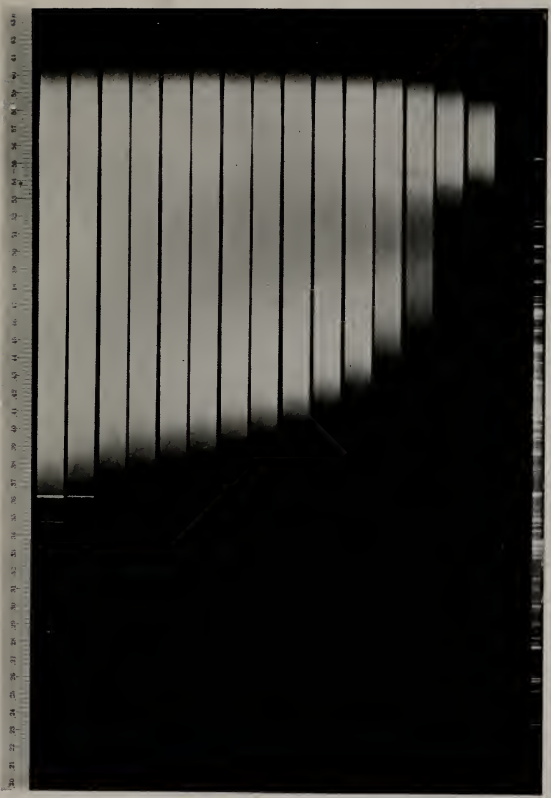
the mother solution transmission began at 0.715 μ, rose to maximum near 0.651 μ, and then decreased to a very small value in the neighborhood of 0.593 μ. Transmission was extremely weak from 0.593 μ to 0.520 μ, *i. e.*, to the beginning of the ultra-violet region of complete absorption. There appeared to be a slight minimum of transmission at 0.575 μ, and a weak maximum at 0.540 μ. Red and orange were, obviously, the only colors appreciably transmitted. The spectrum of the 4 per cent solution was very much like that of the anhydrous solution. The spectra of both solutions agree in having a relatively bright region of transmission in the red, followed by a long, comparatively weak region in the direction of the shorter wave length. The maximum of transmission was near 0.640 μ, and complete extinction commenced at about 0.490 μ. Green and blue were transmitted much more strongly by the 4 per cent solution than by the mother solution. The spectrum of the 8 per cent solution showed that the region of weak transmission had left the green and comprised only the blue. There were no appreciable contrasts in the transmitted regions of the spectra of the remaining solutions in the series. As the percentage of water increased from 0 to 52, the end of the absorption band in the red receded gradually from about 0.715 μ to 0.755 μ.

Copper Bromide in Ethyl Alcohol.—(See Plates XII(*b*) and XIII., which latter is reduced to three-fourths of the original size.) The concentration of the anhydrous mother solution was 0.101. The percentages of water in the series were 36, 32, 28, 26, 24, 22, 20, 18, 16, 14, 12, 10, 8, 6, 4 and 0. Therefore, all the successive differences were equal to 2 per cent except the first 2 and the last 1, and each of these is equal to 4 per cent. Viewed in their bottles, the solutions varied in color from bluish green, through the various shades of green and olive, to very dark brown, as the amount of water decreased from 36 to 0 per cent. The mother solution was sensibly opaque except in very thin layers. The same succession of colors was shown by the solutions when in the the cell at a depth of 0.24 cm., with the exception that the first 4 or 5 solutions appeared practically colorless.

The photographic strips which correspond, respectively, to the solution that contained the greatest amount of water, and to the one that was anhydrous, are adjacent to the numbered scale and to the comparison spectrum of Plate XII. The cell depth for both plates, XII. and XIII., was 0.24 cm. The negative strip belonging to the 36 per cent solution recorded the faintest trace of the cadmium line at 3261.2, but the continuous background became very weak near 0.340 μ. The spectrogram, taken as a whole, shows that the locus of the limit of absorption of the region which included the ultra-violet, was a smooth curve, convex towards the region of shortest wave length. Also the last 6 or 7 photographic strips, show that there was general absorption in the orange and red. The strips corresponding to the solution whose percentages of water were 10, 8, 6, and 4, showed that a region of weak general absorption formed a continuation into the blue and green, of the region of intense absorption of the ultra-violet and violet. The strength of this general absorption increased rapidly as the amount of water in the solutions decreased. This is exactly the same phenomenon as was exhibited by the negatives for the solutions of copper bromide in methyl alcohol and varying amounts of water. The strip corresponding to the anhydrous solution recorded extremely faint transmission from 0.544 μ towards the red.

The negative for Plate XII was taken with a Cramer trichromatic plate. The spectra photographed corresponded to the 5 solutions of the series containing the smallest amounts of water, which included, of course, no water. The depth of the cell was 0.24 cm. The exposures to the light from the Nernst filament were each 2 minutes. The strip nearest to the scales corresponds to the solution which contained 10 per cent of water. The fifth strip, counting away from the scales, pertains to the mother solution. The negative strip corresponding to the 6 per cent solution, recorded the beginning of very faint transmission near 0.451 μ, and showed that relatively intense transmission did not commence until about 0.510 μ. The wave lengths corresponding, respectively, to the beginning of faint and strong transmission,

Plate XIII.

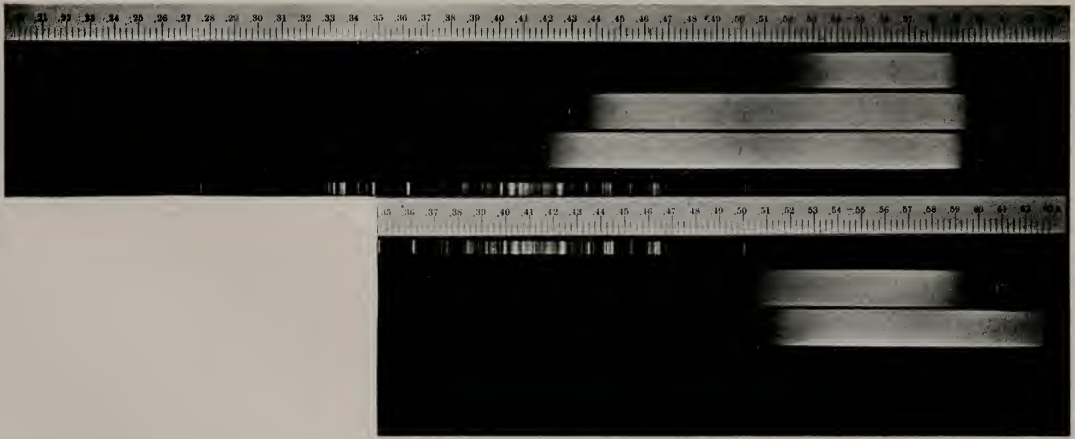


were given as 0.493 μ and 0.533 μ, by the strip for the 4 per cent solution. The mother solution, according to the negative, transmitted very weakly from about 0.538 μ to the end of the field of view of the spectrograph. Eye observations recorded qualitatively the facts revealed by the negative, and also supplemented the latter by giving data for the red end of the spectrum. The depth of cell was, as formerly, 0.24 cm. All light transmitted by the mother solution was very weak, yet the transmission in the red was relatively intense, as compared with that in the yellow and green. More specifically, transmission began at about 0.725 μ, rose to a maximum at 0.653 μ, and then fell to a very small value in the neighborhood of 0.598 μ. Faint light could be observed from 0.598 μ to about 0.518 μ. At the latter wave length absorption became complete. The spectrum transmitted by the 4 per cent solution was similar to that of the mother solution. The yellow and green regions, however, were somewhat stronger, but the blue was very much weakened. The contrast between a relatively bright region of transmission, and a weak region at the more refrangible side of the former, gradually disappeared as the quantity of water in the solutions decreased. The gradations were shown very well by the corresponding negative strips of the spectrogram. For the solution which contained the greatest amount of water the spectrum began near 0.758 μ. The complete series of eye observations showed that the visible end of the absorption band, whose center was in the infra-red, moved towards this region as the percentage of water in the solutions increased.

A series of solutions could not be prepared from copper bromide and acetone, since the latter oxidizes the acetone, and is itself reduced to the cuprous condition and immediately precipitated. The spectrograms, which were taken for the purpose of comparing with one another the absorption spectra of certain solutions of copper bromide in water, in methyl alcohol and ethyl alcohol, are reproduced as Plates XIV(*a*) and XIV(*b*).

Since the mother solutions were too opaque to give satisfactory spectrograms, each was diluted with the proper solvent. The concentrations of the solutions of copper bromide in water, in methyl alcohol and ethyl alcohol were, respectively, 0.874, 0.036, 0.032. When placed in the cell at a depth of 0.24 cm., the solutions in the order given above, were green, light yellow and yellow with a brownish tinge. For Plate XIV(*a*) the strip adjacent to the numbered scale corresponds to the solution in methyl alcohol. The middle strip pertains to the solution in methyl alcohol, and the strip nearest to the spark spectrum corresponds to the aqueous solution. The strip for the ethyl alcohol solution showed that transmission began at about 0.445 μ, and remained comparatively weak as far as 0.527 μ. From this latter point on towards the red, transmission was relatively strong. The negative strip pertaining to the solution in methyl alcohol showed that transmission began near 0.419 μ, and continued intense as far as the limit of sensibility of the photographic film. The negative strip corresponding to the aqueous solution showed that transmisssion began at 0.403 μ, and remained strong to the limit set by the absence of sensitiveness of the film to orange light. The fact that the middle strip extends beyond the adjacent strips at their less refrangible ends, shows that slight general absorption of the orange was exerted by the solutions in ethyl alcohol and in water.

The negative for Plate XIV(*b*) was taken with a Cramer trichromatic plate. The cell depth was 1.75 cm., and each exposure to the light from the Nernst filament was 2 minutes. At this depth the solution of ethyl alcohol had a deep, dull brown color. The solution in methyl alcohol was a deep brownish yellow. The aqueous solution was dark green. The strip adjacent to the scales corresponds to the aqueous solution, the middle strip pertaining to the solution in methyl alcohol as solvent. The negative showed that the ethyl alcohol solution transmitted very weakly from 0.554 μ to the end of the plate. The photographic maximum of transmission was near 0.595 μ. The middle strip showed that the methyl alcohol solution began to transmit at about 0.480 μ, and that transmission was practically complete from 0.510 μ



Plates XIV(a) and XIV(b).

to the end of the field of view of the spectrograph. The negative strip next to the spark spectrum showed that the aqueous solution began to transmit at 0.455 μ, but the brightness of the transmitted light increased very slowly to a maximum in the vicinity of 0.556 μ. Transmission ended at 0.603 μ.

The solutions in question were studied with the spectroscope, the cell having the same depth as for Plate XIV(*b*). The solution in methyl alcohol transmitted red and orange fairly well, but yellow and greenish yellow rather faintly. The spectrum began at 0.705 μ, rose to a maximum at 0.640 μ and then decreased to a region of very weak transmission, which extended from 0.588 μ to 0.543 μ. The methyl alcohol solution transmitted red and orange tolerably well, and yellow quite intensely. The spectrum was relatively weak in the blue. Transmission began at about 0.716 μ, and reached its full value in the neighborhood of 0.610 μ. The intensity decreased from about half its maximum value at 0.525 μ to complete absorption at 0.481 μ. The spectrum of copper bromide in methyl alcohol was very much more intense than that for the solution of the same salt in ethyl alcohol. For the aqueous solution transmission began near 0.636 μ, rose to a maximum at about 0.580 μ, and maintained a comparatively small intensity from 0.520 μ to 0.470 μ. The entire spectrum was a good deal weaker than the spectrum of the methyl alcohol solution, and yet appreciably more intense than the solution in ethyl alcohol.

General Conclusions from Spectrographic Work.

That the absorption spectra of solutions, such as those described in this and in the preceding paper, both separately and when mixed, can throw light on the question of hydration, is readily seen from the following considerations, some of which have already been pointed out:

The phenomenon of absorption, as presented by solutions, is one of resonance. The energy of a vibration of given period, will be absorbed to the greatest extent by a system whose natural period of vibration is most nearly equal to its own.

The period of vibration of a dissolved particle will be *greatly affected by the condensation around it of water molecules—by the formation of hydrates.*

The *more complex the hydrate* in combination with the dissolved particle, the more the vibrations of the particle would be interfered with and, consequently, the *smaller the number of wave lengths with which it would be able to vibrate in resonance.* Therefore, the *solution in which the hydrates were the most complex would have the narrowest absorption bands.*

This conclusion can readily be tested experimentally by means of the absorption spectra. Earlier work in this laboratory has shown that *the more dilute the solution, the more complex the hydrate existing in the solution.* The more dilute solutions should, then, show narrower absorption bands than the more concentrated.

This is shown by Plate II. (p. 162), which represents the spectrograms of a series of solutions of cobalt chloride. The most dilute solution is nearest the numbered scale, and the concentration increases as we go down the plate from the scale. The absorption bands widen out rapidly as the concentration of the solution increases.

Exactly the same relation is brought out by Plate V. (p. 166) for aqueous solutions of copper chloride. The absorption bands widen as the concentration increases; and similar relations come out equally well for copper bromide in water. These are shown by Plate VI. (p. 170), the absorption bands widening rapidly with increasing concentration.

If a solution of a *strong dehydrating agent*, such as calcium chloride or aluminium chloride, is added to an aqueous solution of, say, cobalt chloride, some of the water will be removed from the latter and its particles would be freer to vibrate. The addition of *more and more of the dehydrating agent should, therefore, produce a widening of the absorption bands*, just as increasing the concentration of a solution causes the absorption bands to widen out.

That such is the case is shown by Plate VIII. (p. 172). The solution next to the scale represents pure cobalt chloride. The following strips correspond to solutions containing more and more calcium chloride, the amount of cobalt chloride present remaining constant. It will be observed that the absorption bands widen as the amount of calcium chloride present increases.

The same fact is shown by Plate XIII. (p. 194). The strip next to the scale corresponds to a solution of pure copper chloride, and the succeeding strips to solutions containing more and more calcium chloride. The absorption bands widen with marked regularity.

The absorption spectra of solutions of copper chloride, to which more and more aluminium chloride is added, are shown in Plate XVII. (p. 216), the absorption bands widening regularly with increase in the amount of aluminium chloride.

It will be observed that in Plates VIII., XIII. and XVII. the bands widen, *while the amount of colored salt present remains constant,* and the amount of the colorless salt increases. This shows that there is *no necessary relation between the widening of the bands and the concentration of the colored salt as such.* In order that the bands should widen with increasing concentration, when only the colored salt is present, there must be a change in the hydration of the colored salt.

Let us now turn to solutions of cobalt chloride, copper chloride and copper bromide in such non-aqueous solvents as methyl alcohol, ethyl alcohol and acetone. Take a solution of cobalt chloride in methyl alcohol. In such a solution there can be no hydrate present, since there is no water present; and there is no evidence that the dissolved substance combines with any appreciable amount of the methyl alcohol. In such a solution the dissolved substance, not being weighted down by anything combined with it, would be freest to vibrate in resonance with a large number of wave lengths. The absorption bands should, therefore, be relatively broad. As more and more water is added to the alcoholic solution, the dissolved substance should form more and more complex hydrates, and would be less and less free to vibrate in resonance with any large number of wave lengths. The absorption bands should, therefore, become narrower and narrower as the amount of water present becomes greater and greater.

That such is the case is shown by Plate II. (p. 248). The strip most widely removed from the numbered scale represents the absorption spectrum of cobalt chloride in anhydrous methyl alcohol; and here the bands are the widest. The succeeding strips approaching the scale, represent the solutions of cobalt chloride in methyl alcohol to which more and more water is added. The strip next to the numbered scale corresponds to the maximum amount of water. It will be observed that as the amount of water increases, the absorption bands become narrower and narrower, and are narrowest for the solution containing the maximum amount of water.

The same relation is shown by copper chloride in methyl alcohol. In Plate VII. the lowest strip is the absorption spectrum in pure alcohol. There the absorption is greatest. As more and more water is added to the alcoholic solution, a more and more complex hydrate is formed, which hinders the vibration of the dissolved substance. The absorption bands, therefore, become narrower and narrower as the amount of water present increases.

A study of copper chloride in ethyl alcohol confirms the above conclusion. The strip most remote from the numbered scale of Plate VIII. (p. 259) represents the solution in pure ethyl alcohol. The dissolved molecules are not combined with any appreciable amount of the solvent, and they can, therefore, vibrate freely. They vibrate in resonance with a very large number of wave lengths, and the absorption bands extend nearly across the entire spectrum. As more and more water is added, the molecules of the copper salt become hydrated to a greater and greater extent, and their absorption becomes less and less. This is shown by the rapid narrowing of the absorption bands as more and more water is added to the alcoholic solution.

The above relations repeat themselves for copper chloride in acetone Plate IX. (p. 260). The solution of the pure acetone has the widest bands or greatest absorption, as is shown at the bottom of the plate. The amount of absorption diminishes as the amount of water increases. Indeed, one band entirely disappears after the amount of water present reaches a certain value. Plates XI. and XII. (pp. 263, 264) bring out the same facts for copper bromide in methyl alcohol and in ethyl alcohol. The strips most widely removed from the numbered scales represent the absorption spectra in the pure alcohols. The successive strips, as we approach the scale, represent the addition of more and more water. The hydrates are becoming more and more complex, and the power to vibrate in resonance with many wave lengths less and less. Consequently, the absorption bands are continually becoming narrower and narrower.

If we take into account all of the above evidence from spectroscopic investigation, it seems fair to conclude that this argues very satisfactorily in favor of the present conception of hydrates in aqueous solutions. Attention is called especially to Plates VIII., XIII., and XVII. (pp. 172–194), which show that the widening of the bands is not a function simply of the number of molecules of the colored salt that is present. In order that the absorption bands should widen simply by increasing the concentration of the colored salt alone, it is necessary, as has been shown, for the *hydration of the colored salt to undergo change.* The evidence furnished by solutions in non-aqueous solvents, on addition of water, in favor of the hydrate conception, seems quite as convincing as that obtained from solutions in water itself.

In conclusion, we wish to express our thanks to the Physical Department of this University, for making possible the favorable conditions under which this work was carried out.

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PHYSICAL CHEMICAL LABORATORY,
JOHNS HOPKINS UNIVERSITY,
May, 1906.

Contributions from the Chemical Laboratory of the Nebraska Wesleyan University.

XIV.—STUDIES ON THE SOILS FROM THE NORTHERN PORTION OF THE GREAT PLAINS REGION: THE DISTRIBUTION OF CARBONATES ON THE SECOND STEPPE.

By Frederick J. Alway and Guy R. McDole.

It has been shown by Hilgard[1] that one of the characteristics of the soils of arid regions is the large content of carbonates of calcium and magnesium compared with the soils of humid localities. In the absence of sufficient rainfall to cause percolation through the subsoil, the carbonates, which are dissolved from the surface soil by the rains, accumulate in the subsoil where the last portions of the water are absorbed by the plant roots. It has been found at Rothamsted that the annual loss of calcium carbonate in the drainage water from unmanured plots amounts to about 1000 pounds per acre.[2] At this rate about 200 years would be sufficient for the removal of all the calcium carbonate from 1 foot of subsoil of one of the most important soil types of the steppe, while at the end of 2000 years practically all the calcium carbonate within reach of plant roots would have been removed. Even in the case of the type of soil best supplied with carbonates, 7000 years would have completed the leaching. Assuming that the soils of eastern and western Canada, all of which are of glacial origin, were at first equally rich in carbonates, sufficient time has elapsed since the glacial period to account for the disappearance of these compounds from the soils of the former.

Determinations of carbon dioxide were made in the case of all our samples that formed complete sets to the depth of 6 feet. The 72 samples, the analysis of which is given in Table I., show the distribution as well as the total amount of carbonates occurring in the 2 most fertile types of soil on the second steppe. At many other places than those from which the ones mentioned below were taken, samples of subsoil were obtained, and in all cases were found to contain from 1.50 to 12.00 per cent of carbon dioxide. We find that, in general, there is a tendency for the amount of carbonates to reach a maximum in the second and third foot, or in the portion of subsoil between the second and the fifth foot. In all cases the surface soil is distinctly poorer in carbonates than the subsoil. The most marked regularity in the results, however, is the direct relation between the amount of carbonates and the hygroscopic coefficient of the subsoils. A large content of carbonates is associated with a low hygroscopic coefficient, as is well shown in Table II., in which the results are arranged in the order of the percentage of carbon dioxide.

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[1] Cal. Agr. Expt. Station, Report 1892–94, p. 100.

[2] Hall: Rothamsted Expt., p. 239 (1905).

All samples were obtained by means of a 1.5 inch augur. As each of the samples represents a whole foot section, some of them consist of a mixture of two types of subsoil, where both occurred within the same foot section. The hygroscopic coefficient[1] was determined by exposing a thin layer, 1 mm., of the soil to an atmosphere saturated with water vapor, for 13 hours and afterwards drying at 100° for 24 hours. The coefficient expresses the weight of water held by 100 grams of dry soil. All the fields from which the samples were taken had been under cultivation for many years, with the exception of J, K and L, which were still in virgin prairie. L formed a depression into which the water from the higher (3–6 feet) land of J on the one side and K on the other, each half a mile distant, ran off during very heavy rains. On account of this collection of water over its surface there had been more opportunity for seepage, which evidently had reduced the total amount of carbonate as well as that in the second foot. This field bore a much heavier growth of grass than the adjacent higher land.

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[1] Cal. Agr. Expt. Station, Circular No. 6, p. 13 (1903).

Table I.

Series letter of field.	Locality.	Series number of sample.	Depth of foot section in feet.	Percentage of CO_2.	Hygroscopic coefficient.	Temperature of observation.	Character of soil.
A	Indian Head	1	1	0.63	10.0	15	Lacustral clay.
		2	2	2.57	10.9	"	" "
		3	3	2.23	10.9	"	" "
		4	4	9.46	4.7	"	Boulder clay.
		5	5	9.25	4.9	"	" "
		6	6	9.31	4.5	"	" "
B	Indian Head	7	1	0.42	10.9	"	Lacustral clay.
		8	2	3.38	9.7	17	Lacust. clay and boulder clay.
		9	3	10.26	4.8	"	Boulder clay.
		10	4	8.28	5.4	"	" "
		11	5	8.35	5.5	"	" "
		12	6	8.17	4.4	"	" "
C	Indian Head	13	1	0.21	11.8	20	Lacustral clay.
		14	2	1.84	10.8	"	" "
		15	3	10.20	4.7	"	Boulder clay.
		16	4	8.65	4.4	"	" "
		17	5	9.00	4.4	"	" "
		18	6	8.00	5.2	"	" "
D	Indian Head	19	1	1.70	9.6	10	Boulder clay.
		20	2	9.12	5.6	"	" "
		21	3	11.82	5.6	"	" "
		22	4	9.75	4.5	"	" "
		23	5	6.80	5.8	"	Boulder clay and lacustral clay.
		24	6	6.67	8.7	"	Lacust. clay and boulder clay.
E	Indian Head	25	1	0.65	12.8	10	Lacustral clay.
		26	2	2.24	13.1	"	" "
		27	3	3.80	12.3	"	" "
		28	4	8.60	5.5	15	Boulder clay.
		29	5	8.86	5.5	"	" "
		30	6	7.66	6.6	"	" " and lacustral clay.

Table I—(continued).

Series letter of field.	Locality.	Series number of sample.	Depth of foot section in feet.	Percentage of CO_2.	Hygroscopic coefficient.	Temperature of observation.	Character of soil.
F	Indian Head	31	1	0.46	11.4	12	Lacust. clay and boulder clay.
		32	2	9.51	5.9	"	Boulder clay.
		33	3	9.93	4.6	"	" "
		34	4	8.00	4.3	"	" "
		35	5	7.53	3.9	"	" "
		36	6	7.28	5.0	"	" "
G	Moose Jaw	37	1	Sample lost.			
		38	2	2.22	12.8	15	Lacustral clay.
		39	3	3.21	11.8	"	" "
		40	4	2.87	11.7	"	" "
		41	5	2.77	10.9	"	" "
		42	6	2.70	12.9	"	" "
H	Moose Jaw	43	1	1.28	13.9	17	Lacustral clay.
		44	2	2.05	13.2	"	" "
		45	3	2.25	11.7	"	" "
		46	4	1.97	11.8	"	" "
		47	5	2.96	11.9	"	" "
		48	6	3.19	11.5	"	" "
I	Moose Jaw	49	1	0.83	13.8	11	" "
		50	2	3.04	12.7	"	" "
		51	3	2.97	11.7	"	" "
		52	4	3.00	11.9	16	" "
		53	5	3.18	11.7	"	" "
		54	6	2.63	11.1	"	" "
J	Belle Plaine	55	1	1.25	14.7	13	" "
		56	2	2.58	14.1	"	" "
		57	3	2.50	13.8	"	" "
		58	4	2.36	13.5	14	" "
		59	5	1.90	14.5	"	" "
		60	6	2.23	14.5	"	" "
K	Belle Plaine	61	1	0.82	13.8	14	" "
		62	2	2.63	12.5	"	" "
		63	3	2.34	12.4	"	" "

Table I—(continued).

Series letter of field.	Locality.	Series number of sample.	Depth of foot section in feet.	Percentage of CO_2.	Hygroscopic coefficient.	Temperature of observation.	Character of soil.
K	Belle Plaine	64	4	2.97	11.9	14	Lacustral clay.
		65	5	2.42	13.7	"	" "
		66	6	1.41	14.9	"	" "
L	Belle Plaine	67	1	0.64	14.8	11	" "
		68	2	1.25	14.5	"	" "
		69	3	2.09	14.6	"	" "
		70	4	1.90	14.1	"	" "
		71	5	1.80	13.6	12	" "
		72	6	2.51	13.7	"	" "

Table II.

Series number of sample.	Percentage of CO_2.	Hygroscopic coefficient.	Series letter of field.	Locality.	Character of soil.	Depth of foot section in feet.
13	0.21	11.8	C	I. H.	Lacustral clay.	1
7	0.42	10.9	B	"	" "	1
31	0.46	11.4	F	"	" " and boulder clay	1
1	0.63	10.0	A	"	" "	1
67	0.64	14.8	L	B. P.	" "	1
25	0.65	12.8	E	I. H.	" "	1
61	0.82	13.6	K	B. P.	" "	1
49	0.83	13.8	I	M. J.	" "	1
55	1.25	14.7	J	B. P.	" "	1
68	1.25	14.5	L	"	" "	2
43	1.28	13.9	H	M. J.	"	1
66	1.41	14.9	K	B. P.	"	6
19	1.70	9.6	D	I. H.	Boulder clay.	1
71	1.80	13.6	L	B. P.	Lacustral clay.	5
14	1.84	10.8	C	I. H.	" "	2
59	1.90	14.6	J	B. P.	" "	5
70	1.90	14.1	L	"	" "	4
46	1.97	11.8	H	M. J.	" "	4
44	2.05	13.2	"	"	" "	2

Table II—(continued).

Series number of sample.	Percentage of CO$_2$.	Hygroscopic coefficient.	Series letter of field.	Locality.	Character of soil.	Depth of foot section in feet.
69	2.09	14.6	L	B. P.	Lacustral clay	3
38	2.22	12.8	G	M. J.	" "	2
3	2.23	10.9	A	I. H.	" "	3
60	2.23	14.5	J	B. P.	" "	6
26	2.24	13.1	E	I. H.	" "	2
45	2.25	11.7	H	M. J.	" "	3
58	2.36	13.6	J	B. P.	" "	4
65	2.42	13.7	K	"	" "	5
57	2.50	13.9	J	"	" "	3
72	2.51	13.7	L	"	" "	6
2	2.57	10.9	A	I. H.	" "	2
56	2.58	14.2	J	B. P.	" "	2
54	2.63	11.1	I	M. J.	" "	6
62	2.63	12.5	K	B. P.	" "	2
42	2.70	12.9	G	M. J.	" "	6
41	2.77	10.9	"	"	" "	5
63	2.84	12.4	K	B. P.	" "	3
40	2.87	11.7	G	M. J.	" "	4
47	2.96	11.9	H	"	" "	5
51	2.97	11.7	I	"	" "	3
64	2.97	11.9	K	B. P.	" "	4
52	3.00	11.9	I	M. J.	" "	4
50	3.04	12.7	"	"	" "	2
53	3.18	11.7	"	"	" "	5
48	3.19	11.5	H	"	" "	6
39	3.21	11.8	G	"	" "	3
8	3.38	9.7	B	I. H.	Lacustral clay and boulder clay	2
27	3.80	12.3	E	"	Lacustral clay.	3
24	6.67	8.7	D	"	Lacustral clay and boulder clay	6
36	7.28	5.0	F	"	Boulder clay.	6
35	7.53	3.9	"	"	" "	5
30	7.66	6.6	E	"	Lacustral clay and boulder clay	6
34	8.00	4.3	F	"	Boulder clay.	4
18	8.00	5.2	C	"	" "	6
12	8.17	4.4	B	"	" "	6
10	8.28	5.4	"	"	" "	4
11	8.35	5.5	"	"	" "	5
28	8.60	5.4	E	"	" "	4

Table II—(continued).

Series number of sample.	Percentage of CO_2.	Hygroscopic coefficient.	Series letter of field.	Locality.	Character of soil.	Depth of foot section in feet.
16	8.65	4.4	C	I. H.	Boulder clay	4
29	8.86	5.5	E	"	" "	5
17	9.00	4.4	C	"	" "	5
20	9.12	6.6	D	"	" "	2
5	9.25	4.9	A	"	" "	5
6	9.31	4.5	"	"	" "	6
4	9.46	4.7	"	"	" "	4
32	9.56	5.9	F	"	" "	2
22	9.75	5.6	D	"	" "	4
33	9.93	4.6	F	"	" "	3
15	10.20	4.7	C	"	" "	3
9	10.26	4.8	B	"	" "	3
21	11.82	5.8	D	"	" "	3

The amount of carbonates in the surface soils is, in all cases, less than that in the subsoil. The subsoil, judged by the content of carbon dioxide, is of 2 distinct types, the one carrying from 7.5 to 12 per cent and the other from 1.25 to 4.0 per cent. These two types of subsoil differ in physical as well as in chemical properties. The first, boulder clay, carries stones and boulders, while in the second, a clay of lacustral origin, only an occasional small stone is found. The former readily disintegrates in contact with water, from 1 to 3 hours' boiling being sufficient to reduce it to clean, single grains, as observed under the microscope, while the latter, when treated with water, breaks up into small aggregations, which, when rubbed with a stirring rod, become like putty, and which require from 30 to 36 hours' boiling with water to completely resolve them into their individual soil particles. The till or boulder clay possesses a much lighter color, both in the wet and in the dry condition, than the lacustral clay. The dried lumps of the former can be crushed between the thumb and finger, while those of the latter cannot. As is shown by the table of mechanical analysis, the till is much richer in sand and poorer in clay particles than the lacustral deposit; the proportion of silt in the two is about the same. The difference in appearance of the two types of soil, when removed from fields in which a crop of grass or some cereal has just reached maturity, is very marked, the till being brought to the surface by an augur in the form of a powder, resembling wood ashes, while the other forms a more or less coherent mass of small aggregations. One of the most important and characteristic properties in which the 2 types differ is the hygroscopic coefficient of the subsoil. The surface soil, on account of the humus it contains, possesses a high coefficient, no matter to which type it belongs. In the case of the subsoils that of the till has a value between 3.9 and 6.0, and that of the lacustral clay lies between 10.3 and 14.7. The samples, whose coefficient lay between 5.8 and 10.8, were very few in number, *viz.*, 8, 24 and 30; a careful examination showed that they consisted of mixtures of the 2 types, as was to be expected from the percentage of carbon dioxide.

Table III.

Mechanical Analysis of Specimens of the Two Soil Types.

	Series No. 9. Boulder clay. Per cent.	Series No. 26. Lacustral clay. Per cent.
Gravel, 2.0 to 1.00 mm.	1.7	0.0
Coarse sand, 1.0 to 0.5 mm.	5.2	0.01
Medium sand, 0.5 to 0.25 mm.	5.6	0.01
Fine sand, 0.25 to 0.10 mm.	14.1	2.2
Very fine sand, 0.10 to 0.05 mm.	12.3	6.7
Coarse silt, 0.05 to 0.016 mm.	16.2	19.0
Fine silt, 0.016 to 0.005 mm.	19.5	22.6
Clay, 0.005 to ?	26.1	48.2
Total	100.7	98.8

All the samples from Moose Jaw and Belle Plaine are of lacustral clay; at Indian Head, fields D and F, at the spots where borings were made, are of boulder clay, while fields A, B, C and E are of lacustral clay to a depth of from 1.5 to 3 feet, below which is boulder clay. In both D and E a layer of rather stiff clay, resembling the lacustral deposit, was found at a depth of about 5 feet. In the tables this is referred to as lacustral clay. As its resemblance to the surface deposit was recognized only after the hygroscopic coefficient and carbon dioxide had been determined, no careful examination was made in the field. In most of the fields examined on the Indian Head Experimental Farm the surface soil seemed to consist of a mixture of the 2 types. This is probably due to a combination of 3 causes, *viz.*, (1) high winds, which blow soil from the surface of one type over the surface of the other; (2) the action of the plow where the layer of lacustral clay is very shallow; (3) the work of burrowing animals which carry boulder clay subsoil to the surface and deposit it upon the lacustral clay.

Mr. C. E. Vail, of this laboratory, made carbon doxide determinations of the 4 portions into which the finer material of the till may readily be separated by mechanical analysis. As was to be expected, very little carbon dioxide was obtained from the clay portion.

	Sands.	Coarse silt.	Fine silt.	Clay.
Per cent of CO_2	4.59	12.41	9.08	0.29

Summary.

1. All soils from the second steppe are well provided with carbonates, the subsoils containing more than the corresponding surface soils.
2. Subsoils of boulder clay are much richer in carbonates than those composed of clay of lacustral origin.
3. The carbonates are present chiefly in the soil grains of intermediate size, *viz.*, the silts.
4. A high percentage of carbonates is associated with a low hygroscopic coefficient.

UNIVERSITY PLACE,
NEBRASKA,
July, 1906.

NOTE.

The Generation of Oxygen from Sodium Peroxide.

In a recent note[1] a method is described for lessening the violence of the action of water on fused sodium peroxide in the generation of oxygen. Sodium sulphate, or carbonate crystals, mixed with the peroxide, supply the necessary water. On warming, oxygen is regularly evolved. A similar way of overcoming the difficulty, that may, in certain cases, prove more convenient, is to use an aqueous solution of caustic alkali instead of water alone. Place a lump of the peroxide on a piece of copper gauze, in a dry, round-bottomed flask and add, by means of a dropping funnel, the alkali solution of strength about 1:1. I have used exhausted nitrometer solution. Oxygen is evolved without the need of external heating, and the rate of evolution is sufficiently regular for most purposes.

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[1] THIS JOURNAL, 37, 106 (1907).

George H. Burrows.

University of Vermont.

OBITUARY.

DMITRI IVANOWITSH MENDELÉEFF.

The death of Mendeléeff, in his seventy-third year, has just been announced.

Dmitri Ivanowitsh Mendeléeff was born February 7, 1834, at Tobolsk, Siberia, and died in St. Petersburg, February 2, 1907. He was educated at the gymnasium at Tobolsk and in the scientific department of the Pedagogical Institute at St. Petersburg, an institution for the training of gymnasium teachers. He had a brief period of activity as a teacher, and then took the degree of *Magister Chemiae* at the St. Petersburg University, in 1856. After a stay of 2 years at Heidelburg, he became Professor of Chemistry at the Technological Institute at St. Petersburg and, in 1866, was made Professor of Chemistry at the University of St. Petersburg.

Mendeléeff was a very prolific writer and worked in every field of chemical science. He contributed to our knowledge of mineralogy and chemical geology and carried out several noteworthy researches in organic chemistry. In 1863 he published the first Russian encyclopedia of Technical Chemistry. His influence on the Russian petroleum industry has been all-important. Twenty years ago the petroleum industry of Baku was a monopoly with limited trade and unprogressive management. Thanks largely to the action of Mendeléeff, both on the platform and in the press, the exploitation of this boundless supply was thrown open to the world, with results of the greatest industrial and political importance.

Mendeléeff's reputation rests mainly on his contributions to physical chemistry and to chemical philosophy; among the more important of these are his researches on Specific Volumes, which were stimulated by the work of Kopp, commenced while he was a student in 1855 and continued until

1870; his work on Contact Action, on Fractional Distillation, on the Heat of Combustion of Organic Substances, and on Solution. Much of his activity since 1871 has been given to extended work on the Elasticity of Gases, in collaboration with several of his pupils. Portions only of this work have been published.

Mendeléeff was noted as an inspiring teacher. Two generations of Russian chemists owe their training to him. His treatise on Organic Chemistry was the standard work of its time; his "Principles of Chemistry," first printed in 1869, has passed through 7 editions in Russia and 3 in England. It is a veritable treasure-house of ideas, from which investigators have constantly borrowed suggestions for new lines of research. In it Mendeléeff developed the great generalization known under the name of the "Periodic Law."

It is as the author and expounder of the Periodic Law that Mendeléeff's name is familiar to every student of chemistry, and doubtless his fame in the future will rest chiefly on this basis. He first called attention to the principles on which this law is based in a paper read to the Russian Chemical Society, in 1869. From that time to the present day many chemists, in lectures and in print, have taught that the law can only find its explanation in the Pythagorean theory of an ultimate unity of matter. It is well to again call the reader's attention to what Mendeléeff himself says on this subject.

In his Faraday Lecture, delivered to the English Chemical Society, June 4, 1889, Mendeléeff has indicated the lines on which the evolution of this theory proceeded; that it was based wholly on experiment, that without the knowledge of certain data it could not possibly have been discovered, that with this knowledge its appearance is natural and intelligible. In Mendeléeff's words "the law was the direct outcome of the stock of generalizations of established facts which had accumulated by the end of the decade 1860–1870." He indicates the bearing of the law on the doctrine of constant valency, and on the conception of a primordial matter and continues, "the Periodic Law, based as it is on the solid and wholesome ground of experimental research, has been evolved independently of any conception as to the nature of the elements; it does not in the least originate in the idea of an unique matter, and it has no historical connection with that relic of the torments of classical thought; and, therefore, it affords no more indication of the unity of matter, or of the compound nature of the elements, than do the laws of Avogadro and Gerhardt, or the law of specific heats, or even the conclusions of spectrum analysis."

Mendeléeff was the recipient of honors throughout the chemical world. To mention only a few, he was Honorary Member of the Chemical societies of Germany and America; Foreign Member of the Chemical Society (London) and of the Royal Society; Foreign Associate of the National Academy of Sciences; Member of the Royal Academy of Sciences, Crakow; Honorary President of the Russian Physical-Chemical Society. He received the Davy and Copley medals from the Royal Society and the Faraday medal from the Chemical Society.

The reader who wishes to learn more of Mendeléeff's lifework should turn to Thorpe's excellent study in "Essays in Historical Chemistry," from which most of the material for this notice is taken.

REPORT.

Oxides of the Alkali Metals.

Some of the higher oxides of the alkali metals have been previously studied and are well known. Recently, Rengade[1] has extended our knowledge of these oxides.

The oxides of caesium, rubidium, potassium and sodium, of the composition M_2O, corresponding to the common hydroxides, MOH, hitherto have remained unknown, all attempts to isolate them having failed. Beketoff[2] claims to have made rubidium oxide, Rb_2O, by oxidizing rubidium in a current of air to a mixture of oxides, and reducing this mixture to the monoxide by heating it with rubidium in an atmosphere of nitrogen. Later observers could not confirm these results. Rengade[3] has prepared the oxides by a simple method. He brings a weighed amount of metal into a tube, creates a vacuum in the tube and admits a measured volume of oxygen, which is less than the calculated volume required to oxidize the metal to the oxide, M_2O. After combination, the excess of metal is distilled off, leaving the non-volatile oxide. Caesium reacts violently with oxygen and becomes incandescent, rubidium less violently, while with potassium and sodium heat was required to start the reaction.

Caesium oxide, Cs_2O, is an orange-red, crystalline substance; when heated in a vacuum the color changes, with increasing heat, to carmine-red, to purple, and to black at 150°. On cooling, the color phases are reversed. The oxide reacts violently with water, $Cs_2O + H_2O = 2CsOH$. Between 400°

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[1] C. r., 140, 1536; 142, 1533.

[2] Beketoff: Bull. Acad. St. Petersburg, 1, 174 (1894).

[3] Rengade: C. r., 143, 592, 1152.

and 500° the monoxide decomposes into caesium dioxide and caesium, $2Cs_2O = Cs_2O_2 + 2Cs$.

The last reference given above is a brief note announcing the preparation of the monoxides of rubidium, potassium and sodium. The first is yellow, the last two are white.

E. RENOUF.

REVIEWS.

CHEMICAL ABSTRACTS. Edited by W. A. NOYES and C. E. WATERS, Easton, Pa.: American Chemical Society. Vol. I, No. 1, January 1. 1907. Published semi-monthly. Price, $6.00 per annum.

The appearance of a journal, in the English language, devoted wholly to abstracts of chemical papers, is a most noteworthy event and one that may have an extremely important influence on chemistry throughout the world. It is a distinct challenge to German leadership.

The first thought which its appearance brings is one of regret that it has not been found possible to arrange for an abstract journal issued jointly by the Chemical Society (London), the Society of Chemical Industry and the American Chemical Society, so as to prevent the extravagant waste of time, money and energy involved in the duplication of abstracts. It is tolerably well known that negotiations with this object were opened by the American Society, and that their failure was not due to any lack of effort on its part.

In judging of the degree of success which the editors have attained, it is necessary to compare "Chemical Abstracts" with the "Chemisches Central-Blatt," because the abstracts in the journals of the two English societies do not profess to be complete, but to deal only with pure and applied chemistry, respectively. The "Central-Blatt" is issued weekly and costs $16.00, but, in all probability, the price will be again raised next year. It is not complete and very many abbreviations are used. It is, of course, in the German language, and is subscribed for by only one-half (1600) of the members of the German Chemical Society. As stated above, "Chemical Abstracts" is issued semi-monthly, costs $6.00, is more complete than the German journal, the contents are free from irritating contractions, and are much more conveniently arranged. It is issued to all the members of the American Chemical Society, who now number more than 3000. In these circumstances it is difficult to see why English-speaking chemists should continue to subscribe to the "Central-Blatt." Under the Editor and Associate Editor, there are over 120 Sectional

Editors and Abstractors in charge of the following departments: APPARATUS; RADIOACTIVITY; ELECTROCHEMISTRY; PHOTOGRAPHY; INORGANIC CHEMISTRY; ANALYTICAL CHEMISTRY; MINERALOGICAL AND GEOLOGICAL CHEMISTRY; METALLURGY; ORGANIC CHEMISTRY; BIOLOGICAL CHEMISTRY; FOODS; NUTRITION; WATER, SEWAGE, SANITATION; SOILS AND FERTILIZERS; FERMENTED AND DISTILLED LIQUORS; PHARMACEUTICAL CHEMISTRY; ACIDS, ALKALIES, SALTS; GLASS AND POTTERY; FUEL, GAS, COKE; CELLULOSE AND PAPER; EXPLOSIVES; DYES, BLEACHING AND TEXTILE FABRICS; PIGMENTS, RESINS, VARNISHES, INDIA RUBBER; FATS, FATTY OILS AND SOAP; SUGAR, STARCH AND GUMS; LEATHER; PATENTS.

It will be seen from the above brief outline that the American Chemical Society and the Editorial Staff have done their part well; it only remains for English-speaking chemists all over the world to show their appreciation of the efforts which have been made by subscribing for "Chemical Abstracts," or, better still, by becoming members of the American Chemical Society; the dues are only $8.00 per annum and members receive, without further charge, both the Society's "Journal" and "Chemical Abstracts." J. B. T.

LA GRANDE INDUSTRIE CHIMIQUE. Les Acides. Chlorhydrique, Azotique, Sulfurique (sulphate de sodium et eau régale), et les Chlorures décolorants (eau de Javel, eau de Labarraque, chlorure de chaux) par H. PÉCHEUX, Professeur de chimie a l'école nationale d'arts et métiers d'Aix. Paris: J. B. Baillière et Fils. 1906. pp. 96. Price, $1.50.

This is one of a series of publications on chemical industry. The present volume would be a useful little handbook had technical chemistry not advanced in the last 20 years. The text and illustrations are satisfactory as far as older methods are concerned.

In a review of the preceding volume of the series,[1] it was pronounced incomprehensible that a respectable publisher should dare offer the volume to the public, but it was suggested that it might be an unrevised reprint of an older work; that this excuse cannot be offered is shown by the description, in the present book, of Knietsch's contact process for making sulphuric acid.

The omissions in this volume are as remarkable as in the preceding one. The action of sulphuric acid on salt is the only technical process given for making hydrochloric acid. No mention is made of electrolytic methods for preparing chlorine or for making bleaching powder! The following table[1] gives the relative percentage of bleaching powder made at the present time by the electrolytic and the old methods in different countries.

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[1] THIS JOURNAL, 36, 220.

	Electrolysis. Per cent.	Older methods. Per cent.
Germany	65	35
England	18	82
France	19	81
United States	100	0
Austria	66	34
Spain and Italy	100	0
Russia	55	45
Belgium	54	46

Considering that 19 per cent of French bleaching powder is made by the electrolytic method, failure to mention the process needs no comment. E. R.

ANLEITUNG ZUR VEREINFACHTEN ELEMENTARANALYSE. By PROFESSOR M. DENNSTEDT, Direktor des Chemischen Staats-Laboratoriums in Hamburg. Second Edition. Hamburg: Otto Meissner. 1906. pp. 100. Price, M. 2.40.

Dr. Dennstedt's efforts on behalf of simplified elementary analysis are at last beginning to bear fruit; during the past 2 or 3 years hardly a month has elapsed without the publication of at least one paper on the subject, and some of the processes which have been suggested are actually in use in a few university laboratories! As is well known, Dennstedt's method consists, primarily, in the employment of finely divided platinum instead of copper oxide for the oxidation of volatile material. This is contained in a short tube, and effects a relatively enormous saving of gas and time, the latter being especially marked when the duplex oxygen supply is used. The experience of the method, gained since the book was first published, has been utilized, to amend, in the present edition, the descriptions of apparatus and procedure and to introduce a number of improvements in detail, but, fundamentally, the process has not been either complicated or modified.

Professor Dennstedt is to be congratulated on the success of the first edition of his book, and it may be confidently anticipated that an even greater measure of favorable recognition will be accorded to the present issue. In the preface the author urges all who have difficulty with this method

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[1] Hasenclever: Chem. Ind., 28, 52, quoted in Jahrbuch Chem., 1905, 373.

of analysis to communicate directly with him; suggestions in regard to it will be welcomed and he will gladly analyze any substances with which the copper oxide method is unable to cope.
J. B. T.

VORLESUNGEN ÜBER ANORGANISCHE CHEMIE FÜR STUDIERENDE DER MEDIZIN. Von DR. ERNST COHEN und DR. P. VAN ROMBURGH, Ordentliche Professoren an der Reichsuniversität zu Utrecht. Mit 68 Figuren nach Originalphotogrammen. Leipzig: Wilhelm Engelmann. 1906. pp. 431. Price, M. 15.

This is a text-book of inorganic chemistry of medium length, written in chapters called "lectures," although they are far too long to be actually used as such without subdivision. The reason offered by the authors for this arrangement is as follows:

"Those who know the great difficulties which the study of chemistry presents to the beginner, know that the desired result can only be reached by a 'frappez fort, frappez toujours.' As the material in this book is in the form of lectures, opportunity is given to bring the chief facts repeatedly before the student. To attain this result we have, in connection with a given substance, described the chief phenomena and the laws governing them at length, so that what has been thus learned may be easily applied to substances studied later, and we have not hesitated to repeat the explanation of the most important principles at suitable opportunity. For this reason more space is given to the fundamental laws of general chemistry than is usual in works designed for the same purpose as this."

On examining the book we find that the earliest substance treated of is water, and in the first 5 lectures, occupying 65 pages, the authors bring in (a propos of water) nearly all the theoretical chemistry they need, including, among other matters, atomic and molecular theories, vapor density determinations, reversible reactions, electrolytic dissociation, acids, bases and salts, acidimetry, alkalimetry and titration, endothermic and exothermic reactions, dissociation of gases, chemical equilibria, solution of gases and Henry's law. All this before the study of a single element! The sixth lecture takes up the study of oxygen and the remainder of the book, with a few exceptions, is purely descriptive. Practically, then, we find here the old German text-book arrangement; an opening section with theory, the rest descriptive. The book seems to be a hard one to study. The periodic system is dismissed in a few lines on the last 2 pages of the book as unsatisfactory, consequently the practical help in classification which it affords the student is lost. Why the book should be especially for students of medicine is not clear. There are no more references to properties of substances useful in medicine than in the average text-book.

On the other hand, it must be recognized that the book is very clearly and thoughtfully written, and that the medical student who succeeds in mastering it will have a respectable knowledge of chemical laws and of inorganic chemistry.

E. R.

JAHRBUCH DER CHEMIE. Bericht über die wichtigsten Fortschritte der reinen und angewandten Chemie. Herausgegeben von RICHARD MEYER. XV Jahrgang, 1905. Braunschweig: F. Vieweg und Sohn. 1906.

This new volume of the *Jahrbuch* covers 595 pages. The list of co-workers is the same as last year, with the exception of Professor Werner, who has given up the review of inorganic chemistry. His place is filled by the well-known inorganic chemist, Professor K. A. Hofmann, of Munich.

The value of the *Jahrbuch* is so well established that it is only needful to say that the present volume maintains the standard of thoroughness of its predecessors. E. R.

DER NACHWEIS VON SCHRIFTFÄLSCHUNGEN, BLUT, Sperma, u. s. w. unter Besonderer Berucksichtigung der Photographie. Von PROF. DR. M. DENNSTEDT und DR. F. VOIGTLÄNDER. Braunschweig: Friedrich Viewig und Sohn. 1906.

A work by the same authors, bearing upon the same general subject, was recently reviewed.[1] The present volume deals with the detection of adulterations in handwriting, with special reference to the use of photography. The technique of the processes is described in full, and numerous micro-photographical representations of fraudulent handwriting are used to exemplify the methods given. The question of the obliteration of the original handwriting is treated in detail and especially the bleaching materials which are employed. Imitations of handwriting are dealt with at great length and in detail, both by chemical and photo-microscopical processes. An interesting chapter is devoted to the micro-chemical examination of blood spots and of thumb prints. Analysts and experts will find this book extremely helpful, especially in the preparation of photographs for forensic purposes.

H. W. WILEY.

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[1] THIS JOURNAL, 36, 221 (1906).

AN ELEMENTARY STUDY OF CHEMISTRY. By WILLIAM MCPHERSON, PH.D., Professor of Chemistry, Ohio State University, and WILLIAM EDWARDS HENDERSON, PH.D., Associate Professor of Chemistry, Ohio State University. Revised Edition. Boston and New York: Ginn & Co. 1906.

This manual has been in use—in privately printed form—for 3 years at the Ohio State University. After such revision as experience suggested, it is now offered to the public. It is a book of the size and scope of Remsen's "Briefer Course," and contains at the close a chapter on simple organic compounds.

At first sight the book would seem not to differ essentially from several other manuals, but a close examination shows that it is written with marked ability and great care. The chapter on molecular and atomic weights and other chapters on theory are remarkably good and clear. The dissociation theory is applied throughout the book wherever it serves to explain phenomena; the older definitions of acids, bases and salts are replaced by definitions in terms of the theory.

While the descriptions of technical methods are necessarily very brief, they are modern and accurate.

The book can be cordially recommended as an excellent manual for high schools and for elementary college work.

E. R.

VOL. XXXVII. APRIL, 1907. NO. 4.

AMERICAN

CHEMICAL JOURNAL

Contribution from the Kent Chemical Laboratory of the University of Chicago.

ON THE BEHAVIOR OF SODIUM AND SODIUM ALCOHOLATES TOWARDS VARIOUS ESTERS OF ACETIC ACID.

BY LOUIS ALLEN HIGLEY.

An exhaustive study, covering a period of over 10 years, by Nef[1] of the primary and secondary alcohols, their salts and ethers, has proved that all these compounds are partially dissociated into alkylidene and water or metallic hydroxide, respectively,

$$RR'CHOM \rightleftarrows RR'C\langle + HOM$$

$$[R \text{ and } R' = C_nH_{2n+1}, C_{n'}H_{2n'+1}, C_6H_5 \text{ or } H;$$

$$M = H, C_nH_{2n+1}, \text{ or a metal}];$$

furthermore, all primary and secondary alkyl halides, sulphates, nitrates, etc., have been shown by Nef[2] to be similarly dissociated according to

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[1] Ann. Chem. (Liebig), **298**, 202–374; **318**, 137–230; **335**, 191–333.

[2] *Ibid.*, **309**, 126–189; **310**, 316–335; **318**, 1–57.

$$\mathrm{RR'CHX} \rightleftarrows \mathrm{RR'C}< + \mathrm{HX}$$

$$[\mathrm{X} = \mathrm{Cl, Br, I, ONO_2, OCOCH_3, {}^1/_2SO_4}, \text{etc.}].$$

The only difference is that the percentage of dissociation which exists at ordinary temperatures in the substances named varies (1) with the nature of the alkyl radical, and (2) with the nature of X or of OM.

It follows from this that all the known reactions of the primary and secondary alkyl halides, etc., with ammonia, benzene, etc., and with salts of various substances, such as acetic acid, acetoacetic ester, etc., can no longer be interpreted from the standpoint of metalepsis, but depend upon the fact that alkylidene dissociation exists to a greater or less degree in the various reagents used; the speed of the reaction in a given instance must, obviously, be directly proportional to the amount of existing dissociation. Thus, when sodium acetoacetic ester reacts with ethyl iodide, nitrate, or sulphate to give α-ethyl acetoacetic ester and sodium iodide, nitrate or monoalkyl sulphate, respectively, the reaction proceeds in successive stages, as follows: The HX

$$[\mathrm{X} = \mathrm{I, ONO_2} \text{ or } \mathrm{OSO_2OR}]$$

present as a product of dissociation acts on sodium acetoacetic ester,

$$\mathrm{CH_3C(ONa) : CHCOOR},$$

forming NaX and setting free acetoacetic ester, which is then absorbed at once by the alkylidene according to

$$\mathrm{CH_3CH}< + \mathrm{H{-}C(COOR) : C(OH)CH_3} \rightarrow \mathrm{CH_3CH_2{-}C(COOR) : C(OH)CH_3}.$$

This reaction, therefore, belongs to the category of alkylidene condensations;[1] and the enormous number of analogous carbonyl and ethylene condensations observed in the last 18 years, especially by Michael, Auwers, Knovenagel and Vorländer in the case of acetoacetic ester and allied compounds with aldehydes, ketones, and olefines (in the presence of sodium alcoholates, or traces of primary and secondary amines) must be regarded as important experimental evidence tending to establish the correctness of this interpretation of the reaction.[1] It is interesting to notice that the ethylidene does not absorb acetoacetic ester to give a trace of β-ethoxyisocrotonic ester,

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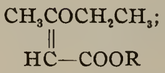
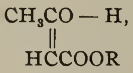
[1] Cf. Nef: Ann. Chem. (Liebig), 298, 202–231.



$$\begin{matrix}\mathrm{CH_3COCH_2CH_3;}\\ \|\\ \mathrm{HC{-}COOR}\end{matrix}$$

furthermore, it is *certain* that this compound is not an intermediate product in the reaction under discussion.

It is important, therefore, to realize that in most of the reactions in which acetoacetic ester or its salt is absorbed by unsaturated compounds, as alkylidenes, olefins, ketones, aldehydes, nitriles, etc., it is *not* the ionic hydrogen atom,



$$\begin{matrix}\mathrm{CH_3CO - H,}\\ \|\\ \mathrm{HCCOOR}\end{matrix}$$

but the *non-ionic* hydrogen atom bound to the α-carbon atom,

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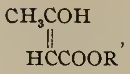
[1] The interpretation of Michael that the ethyl iodide adds itself directly to sodium acetoacetic ester, giving first an addition product, $CH_3C(ONa)ICH(COOR)C_2H_5$, an interpretation which I also formerly adopted (Ann. Chem. (Liebig), **266**, 59–62), is no longer tenable and was given up by me 9 years ago (Ann. Chem. (Liebig), **298**, 263–269). My work since has shown that the long-known reactions of dialkyl sulphides and tertiary amines with alkyl halides which result in the formation of trialkyl sulphinium halides, $R_3 \vdots SX$, and quaternary ammonium halides, $R_4 \vdots NX$, proceed in *three* successive stages (Ann. Chem. (Liebig), **309**, 162–3; **318**, 1–57). There is, consequently, at the present time not a single instance known where an alkyl halide is added directly to an unsaturated compound or atom in the manner assumed by Michael.

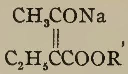
Furthermore, the stable addition products recently described by him (Ber. d. chem. Ges., **38**, 3217), with chloracetic ester, sodium acetoacetic ester and malonic ester do not exist, but have been proved by Paal (Ber. d. chem. Ges., **39**, 1436) to consist simply of a mixture of the alkylated derivative and colloidal sodium chloride. I might mention, that I observed, in 1890, in connection with my experiments with sodium acetoacetic ester and acyl chlorides, that almost clear solutions were at first obtained on mixing the reagents in the presence of ether; this observation, as well as other data, led me to the conclusion, at that time, that addition products of the character assumed by Michael must have been formed. We are obviously, however, dealing here simply with a mixture of sodium chloride in colloidal solution and the acylated derivatives of acetoacetic ester.

The addition products recently mentioned by Bushong and by Willcox (THIS JOURNAL, **30**, 216; **32**, 448; cf. also Ephraim: Ber. d. chem. Ges., **35**, 778; **39**, 1905), and obtained by them from chlorsulphone ethyl ester and sodium alcoholates, in absolute ethereal solution, are obviously also mixtures of ethyl alkyl sulphate and sodium chloride in colloidal solution. J. U. NEF.



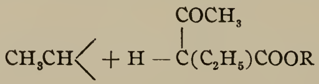
$$\begin{array}{l}CH_3COH \\ \quad\| \\ HCCOOR\end{array},$$

which is torn from the atom to which it is bound. The obvious consequence of this is that the condensation or addition products obtained contain the residue introduced bound to the α-carbon atom of acetoacetic ester.[1] When sodium α-ethyl acetoacetic ester,



$$\begin{array}{l}\quad CH_3CONa \\ \qquad\| \\ C_2H_5CCOOR\end{array},$$

is converted by ethyl iodide, nitrate, or sulphate into α-diethylacetoacetic ester the ethylidene absorbs similarly the *non-ionic* keto-α-ethylacetoacetic ester molecules present



$$CH_3CH\!< + H - \overset{\displaystyle COCH_3 \atop |}{C}(C_2H_5)COOR$$

(cf. foot-note), to give the product,

$$CH_3CH_2C(C_2H_5)(COCH_3)COOR,$$

actually obtained.

It is usually supposed that only alkyl halides can act as alkylating agents, but in view of the new theory of Nef, presented in part above, it is clear that not only these substances but also any compound giving alkylidene by dissociation, can act as an alkylating agent.[2] This explains why the alkyl sulphates and nitrates are so valuable and have so long been used commercially as alkylating agents. It also follows logically from Nef's work that the "cracking" of petroleum

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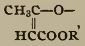
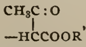
[1] One can also assume that the anion of acetoacetic ester,  $\begin{array}{l}CH_3C{-}O{-} \\ \quad\| \\ HCCOOR\end{array}$, rearranges with great speed into  $\begin{array}{l}CH_3C:O \\ \quad| \\ {-}HCCOOR\end{array}$, and is then absorbed by one affinity unit of an unsaturated compound; this is perfectly analogous to the rearrangement of the anion of nitrous or prussic acid, cf. Ann. Chem. (Liebig), **309**, 150. At the present time, I consider this as the most justifiable interpretation of the reaction and the same idea may also be applied to the aldol condensation. J. U. NEF.

[2] Ann. Chem. (Liebig), **309**, 180.

which results in the splitting as well as in the building up of the carbon chains in the paraffins, is similarly due to alkylidene dissociation, etc. We know from the experiments of Dennstedt[1] that ammonia, pyrrole, primary and secondary amines, phenols, etc., can be alkylated by alcohols in the presence of zinc dust, at 250°. These reactions, as Nef has shown, depend upon an intermediate formation of zinc alcoholate, which must at once dissociate completely, under the existing temperature conditions, into zinc hydroxide and alkylidene, and the latter substance must then absorb the ammonia, phenol, etc., to give the alkylated derivatives which were obtained.

Nef has shown that the metallic alcoholates, $RR'CHOM$, where $M = Ca, Ba, Zn, Na, K$, etc., have very low decomposition points, 200°–250°; consequently, much dissociation, according to $RR_1C\!<\; + HOM$, exists at ordinary temperatures. This explains why the salts of primary and secondary alcohols are spontaneously combustible and also why these substances act as alkylating agents. Thus it has been found that aniline can be alkylated by means of sodium alcoholates at 200°–250°; Nef was also able to prove[2] that when the ionic hydrogen atom is removed or replaced it is possible to alkylate, by means of sodium alcoholates, with especial ease, the α-hydrogen atoms present in acetic acid and its mono- and dialkylated substitution products,

$$CH_3COOM, \qquad RCH_2COOM, \qquad RRCHCOOM.$$

By similar treatment the non-ionic hydrogen atom in formic acid derivatives, $HCOOM$, can be replaced by alkyl (methyl, ethyl, diphenyl methyl) to a slight extent, giving thus the monoalkylated formic acids, $RCOOM$. Nef interpreted his experiments with sodium alcoholates and ethyl acetanilide at 150° on the basis of a direct union of the alkylidene with ethyl acetanilide,

$$RCH\!< + H{-}CH_2CON(C_2H_5)C_6H_5 \Longrightarrow RCH_2CH_2CON(C_2H_5)C_6H_5.$$

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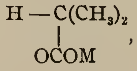
[1] Ber. d. chem. Ges., **23**, 2563–70.

[2] Ann. Chem. (Liebig), **318**, 143–182.

It was, however, obvious from the experiments of Geuther and Claisen, with acetic ester and sodium ethylate, that these reactions might be due to an intermediate formation of acetoacetic ester. This compound would then, naturally, under the conditions of the experiment, 150°, unite at once with the alkylidene present to give the mono- and di-α-alkylated acetoacetic esters; these must then obviously undergo an "acid splitting" in the presence of the sodium hydroxide and thus give rise to the mono- and dialkylated acetic acids obtained by Nef and Geuther in their syntheses. I, therefore, began experiments at once in this direction at the suggestion and under the guidance of Dr. Nef and was soon able to prove an intermediate formation of acetoacetic ester from mixtures of ethyl acetanilide and sodium alcoholates at 100°—so that there is now no doubt that many of these syntheses take place through an intermediate formation of an acetoacetic ester. There are, however, many instances where the alkylation of the acetyl radical takes place directly and still other cases where it is impossible, from the existing evidence, to decide between these two interpretations—which necessarily however, lead to the same end result. The alkylation of a formyl group, as well as of the tertiary hydrogen atom in isobutyl,



$$\begin{array}{l}\mathrm{H-C(CH_3)_2} \\ \quad\;\; | \\ \quad\mathrm{OCOM}\end{array},$$

by sodium alcoholates must, of necessity, take place directly, since the formation of an acetoacetic acid derivative is impossible. These investigations led me, further, to a careful study of the action of sodium and of sodium alcoholates on various esters of acetic acid and a very brief statement of some of my results has appeared in the papers of Beatty and of Bacon.[1] I have also studied the behavior of sodium benzylate towards heat and towards dry oxygen and have proved that it acts as an alkylating agent.

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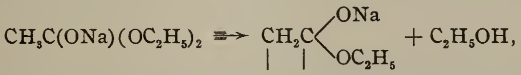
[1] THIS JOURNAL, 30, 225, foot-note; 33, 79-80.

EXPERIMENTAL PART.

Ethyl Acetate and Sodium Ethylate.—It may now be considered as definitely established through Claisen's experiments[1] that sodium ethylate is the active condensing agent when acetic ether is converted into sodium acetoacetic ester by means of sodium. The isolation by Claisen of the addition product, $C_6H_5C(ONa)(OC_2H_5)_2$, proves that here also an analogous ortho derivative must first be formed, which then, according to his former interpretation, splits off 2 molecules of alcohol by metalepsis with a second molecule of acetic ester,

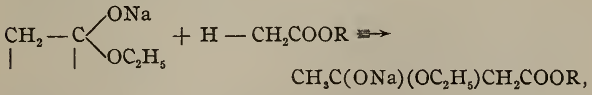
$$\mathrm{CH_3C(ONa)(OC_2H_5)_2 + H_2CHCOOR \rightarrow CH_3C(ONa) : CHCOOR + 2C_2H_5OH},$$

giving thus sodium acetoacetic ester. Nef has shown[2] that this reaction should be classed among the olefin condensations, *i. e.*, that the ortho addition product first formed loses 1 molecule of alcohol,



$$\mathrm{CH_3C(ONa)(OC_2H_5)_2} \rightarrow \underset{|}{\mathrm{CH_2}}\underset{|}{\mathrm{C}}\left\langle\begin{matrix}\mathrm{ONa}\\ \mathrm{OC_2H_5}\end{matrix}\right. + \mathrm{C_2H_5OH},$$

giving thus sodium *iso*acetic ester, which then immediately absorbs a second molecule of acetic ester,



$$\underset{|}{\mathrm{CH_2}}-\underset{|}{\mathrm{C}}\left\langle\begin{matrix}\mathrm{ONa}\\ \mathrm{OC_2H_5}\end{matrix}\right. + \mathrm{H-CH_2COOR} \rightarrow \mathrm{CH_3C(ONa)(OC_2H_5)CH_2COOR},$$

giving as the end product, by further loss of 1 molecule of alcohol, sodium acetoacetic ester. The reaction is, furthermore, as Nef has first pointed out, reversible, and this explains most simply the so-called "acid splitting" of acetoacetic ester, as well as of its mono- and di-α-alkylated substitution products.

E. von Meyer and Friessner[3] have recently studied the action of sodium ethylate on ethyl acetate at various temperatures and found that the maximum yield of sodium acetoacetic ester is only 36.1 per cent of that demanded by the theory after 2 hours' heating at 100°. They found, further, that temperatures above 140° depress the yield most strikingly and that only small yields are obtained at ordinary temperatures. On account of the last named observation, and because metallic sodium gives with acetic ester a relatively larger yield of sodium acetoacetic ester at ordinary temperatures, Michael[1] still disputes the conclusion of Claisen that sodium ethylate is the active condensing agent in the reaction under discussion. He assumes that acetic ester and sodium first give hydrogen and sodium acetic ester according to

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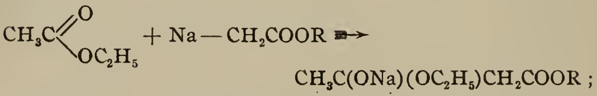
[1] Ber. d. chem. Ges., **20**, 636; cf. Ann. Chem. (Liebig), **297**, 92–8.

[2] Ann. Chem. (Liebig), **298**, 320.

[3] J. prakt. Chem. [2], **65**, 528.

$$H{-}CH_2COOR + Na \rightarrow NaCH_2COOR + H,$$

and that sodium acetic ester is thereupon absorbed by acetic ester,



$$CH_3C\begin{matrix}{/\!\!/}O\\ \diagdown OC_2H_5\end{matrix} + Na{-}CH_2COOR \rightarrow CH_3C(ONa)(OC_2H_5)CH_2COOR\,;$$

the addition product thus formed must then give, by loss of alcohol, sodium acetoacetic ester, as shown above. I have found, contrary to E. von Meyer and Friessner's observations, that mixtures of 36 grams of ethyl acetate (2 mols.) and 10 grams of sodium ethylate, on standing for 7 and for 25 days, respectively, give 5.1 grams and 6.9 grams of pure acetoacetic ester, boiling at 175°–177° (uncor.). The amount in the first case was, therefore, 26.7 per cent and in the second 36.1 per cent of that demanded by the theory. Furthermore, it is well known that dilution with alcohol affects the yield most strikingly. These results show that the reaction between sodium ethylate and ethyl acetate takes place with measurable speed at 20° and reaches the equilibrium point only after about 25 days, whereas, at 100°, according to von Meyer and Friessner's observations, this point is reached after 2 hours. The conclusion, finally, of Michael that metallic sodium reacts *directly* with ethyl acetate to give hydrogen and sodium acetic ester is untenable, (i) because experiments (described below) with sodium and with acetic ester dissolved in 5 parts of absolute ether prove that *no trace* of hydrogen or of sodium acetoacetic ester is formed; (ii) because ethyl butyrate and ethyl caproate give, with metallic sodium, no trace of hydrogen but, almost quantitatively, ketol derivatives[1] according to

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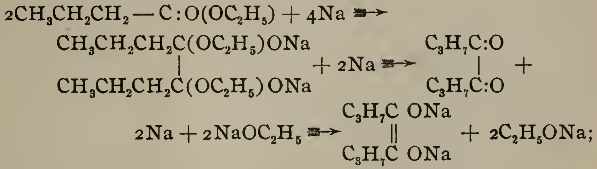
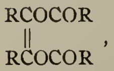
[1] Ber. d. chem. Ges., **33**, 3731 and **38**, 1922; cf. Claisen : Ber. d. chem. Ges., **38**, 709.



$$2CH_3CH_2CH_2—C:O(OC_2H_5) + 4Na \rightarrow \begin{array}{c} CH_3CH_2CH_2C(OC_2H_5)ONa \\ | \\ CH_3CH_2CH_2C(OC_2H_5)ONa \end{array} + 2Na \rightarrow \begin{array}{c} C_3H_7C:O \\ | \\ C_3H_7C:O \end{array} + 2Na + 2NaOC_2H_5 \rightarrow \begin{array}{c} C_3H_7C\ ONa \\ \| \\ C_3H_7C\ ONa \end{array} + 2C_2H_5ONa;$$

and (iii) because propionyl, butyryl and isovaleryl chlorides give, on treatment with metallic sodium, no trace of hydrogen or of an acetoacetic ester-like derivative, but acylated dioxydialkyl ethylenes, which are also ketol derivatives,



$$\begin{array}{c} RCOCOR \\ \| \\ RCOCOR \end{array},$$

and are formed[2] in a manner perfectly analogous to the dialkylated dinatroxyethylenes obtained by Bouveault and Locquin (under ii).

The fact that the monomolecular quantity of ethyl acetate, when diluted with absolute ether, gives, with the diatomic amount of sodium, large quantities of sodium ethylate besides dimethylketol, $CH_3CH(OH)COCH_3$ (see below), but no trace of hydrogen or of sodium acetoacetic ester, is of the greatest importance. It proves, taken in connection with Bouveault and Locquin's results,[3] (i) that an interaction between sodium and acetic ester, according to Michael,

$$H—CH_2COOR + Na \rightarrow NaCH_2COOR + H,$$

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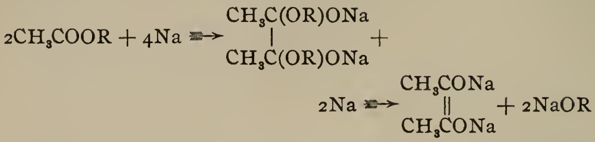
[1] Bouveault and Locquin: Comptes rendus, **140**, 1593. Hantzsch: Ann. Chem. (Liebig), **249**, 54; **246**, 129. Nef: Ann. Chem. (Liebig), **308**, 283-292. Acree: THIS JOURNAL, **29**, 588. Bacon: THIS JOURNAL, **33**, 78.

[2] Klinger: Ber. d. chem. Ges., **16**, 995; **19**, 1863; **24**, 1264; **31**, 1217. Cf. Nef: Ann. Chem. (Liebig), **308**, 283-289.

[3] *Loc. cit.*

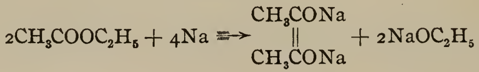
cannot possibly take place; (ii) that a reaction between these reagents takes place according to



$$2CH_3COOR + 4Na \rightarrow \begin{array}{c} CH_3C(OR)ONa \\ | \\ CH_3C(OR)ONa \end{array} + 2Na \rightarrow \begin{array}{c} CH_3CONa \\ \| \\ CH_3CONa \end{array} + 2NaOR$$

and that this is the *only* reaction taking place when an indifferent solvent, like ether, is present to dilute the acetic ether and precipitate the sodium ethylate as soon as it is formed, thus preventing the possibility of the unchanged acetic ester and the sodium ethylate from acting upon each other to give alcohol (2 mols.) and sodium acetoacetic ester according to Geuther and Claisen.

It is, furthermore, exceedingly probable that when undiluted acetic ester is treated directly with metallic sodium—which I understand is the method used in the manufacture of acetoacetic ester—2 entirely independent reactions take place simultaneously, *viz.*, (i) in which the sodium reacts directly with the acetic ester according to



$$2CH_3COOC_2H_5 + 4Na \rightarrow \begin{array}{c} CH_3CONa \\ \| \\ CH_3CONa \end{array} + 2NaOC_2H_5$$

and another reaction in which the sodium ethylate formed in (i) or by the action of sodium on the free alcohol present, reacts at once with the excess of acetic ester present, according to Geuther and Claisen,

$$2CH_3COOC_2H_5 + NaOC_2H_5 \rightarrow CH_3C(ONa) : CHCOOC_2H_5 + 2C_2H_5OH,$$

giving free alcohol and sodium acetoacetic ester. The alcohol thus set free then reacts at once with the sodium present to give hydrogen and sodium ethylate so that the *main reaction* is obviously the formation of sodium acetoacetic ester under these conditions. Both Claisen and Friessner emphasize that the amount of hydrogen set free in the reaction between ethyl acetate and sodium is noticeably less than that demanded by theory, and Claisen, therefore, concludes that some of the atomic hydrogen set free is used up in reducing ethyl acetate. The discrepancy is now self-evident since sodium and ethyl acetate can react upon each other according to reaction (i) without any evolution of hydrogen and with formation of much sodium ethylate. In view of all these considerations it should be more advantageous to manufacture acetoacetic ester from ethyl acetate and alcohol-free sodium ethylate, for under these conditions a reaction can take place only in one direction but not completely, because the reaction is reversible and reaches the equilibrium point when about 36.5 per cent of sodium acetoacetic ester is formed. Furthermore, it is my conviction that the greater yield and ease of action when sodium, instead of sodium ethylate, is used with ethyl acetate—points which are emphasized both by Claisen and by Michael—will, by further investigation, be found capable of a very simple explanation. It follows, for instance, from Nef's work[1] that sodium acetic ester must go over spontaneously, by intramolecular addition, into sodium isoacetic ester; an addition of the hypothetical sodium acetic ester to another molecule of ethyl acetate, as assumed by Michael, is, therefore, in the highest degree improbable.[2]

Ethyl Acetanilide and Sodium Ethylate.—Forty-six and one-half grams of ethyl acetanilide (2 mols), b. p. 148° (31 mm.), and 9.7 grams of sodium ethylate were intimately mixed by shaking in a sealed tube and then heated at 100° for 30 hours, 8 hours daily. The mixture was treated with an excess of dilute sulphuric acid and the oil which separated was extracted with ether, then dried with calcium chloride. On fractionation, 5.7 grams of acetoacetic ester, besides 8 grams of unchanged ethyl acetanilide, boiling at 148°–152° (35 mm.) and 3.4 grams oil boiling above 170° (35 mm.), were obtained. The acetoacetic ester which boiled at 175°–177° (uncor.) was identified by conversion into β-phenylhydrazidoisocrotonic ester and into 1-phenyl-3-methylpyrazolone (6.4 grams, m. p. 127°). The sulphuric acid solution gave, upon making alkaline with sodium hydroxide, 24.9 grams of ethyl aniline boiling at 94°–95° (20 mm.).

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[1] Ann. Chem. (Liebig), **308**, 284.

[2] In his latest papers Michael assumes that sodium reacts on ethyl acetate to give directly sodium isoacetic ether and hydrogen; such an interpretation is now also obviously untenable. I concur, however, with Michael's conclusion that the ethyl acetate absorbs the sodium isoacetic ester (see foot-note above). J. U. NEF.

These results prove that 37 per cent of the theoretical amount of acetoacetic ester was formed according to

$$2C_6H_5(C_2H_5)NCOCH_3 + NaOC_2H_5 \rightarrow CH_3C(ONa):CHCOOR + 2C_6H_5NHC_2H_5;$$

the addition product,

$$CH_3C(ONa)(OC_2H_5)N(C_6H_5)C_2H_5,$$

is, obviously, an intermediate product in this case.

The formation of ethyl,- isobutyl-, and isoamylacetic acids from equal molecules of ethyl acetanilide and the corresponding sodium alcoholates, at 150°–240°, as observed by Nef,[1] must, therefore, be due to an intermediate formation of acetoacetic ester with subsequent alkylation and "acid splitting," as explained in the introduction. It is possible to interpret in a similar manner the reaction of sodium ethylate and sodium acetate, at 200°–210°, alone and in the presence of carbon monoxide, whereby, according to the observations of Geuther and Beatty,[2] mono- and diethylacetic acid are formed. Beatty observed, in connection with these experiments, that on mixing cold alcoholic solutions of potassium acetate and sodium ethylate a very voluminous, crystalline precipitate formed, which was assumed by him to be an ortho addition product, $CH_3C(OK)(ONa)OC_2H_5$.

On repeating the experiment with 1 gram of sodium and 5 grams of potassium acetate and separating the salt, 1.9 grams of fine, silky, white needles were obtained. These were found, however, to consist of pure sodium acetate, as shown by the following analyses:

0.2918 gram substance gave 0.2504 gram Na_2SO_4.

0.3840 gram substance gave 0.2722 gram NaCl.

0.3725 gram substance gave 0.3980 gram CO_2 and 0.1302 gram H_2O.

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[1] *Loc. cit.*

[2] THIS JOURNAL, 30, 242.

0.3252 gram substance gave 0.3444 gram CO_2 and 0.1167 gram H_2O.

	Calculated for $C_2H_3O_2Na$.	Found. I.	II.
Na	28.08	27.82	27.92
C	29.23	29.13	28.87
H	3.70	3.91	4.01

Special experiments with sodium ethylate and sodium acetate, as well as with the corresponding potassium salts, have shown decisively that no union to form an ortho addition product took place at the ordinary temperature. The fact that acetic anhydride and sodium acetate react more energetically as an acylating agent than either reagent separately—as well as the observation of Perkin, Sr., that these reagents, when heated to 180°, give carbon dioxide and acetone, also points to an intermediate formation of an acetoacetic acid derivative and, therefore, also of an ortho addition product, $CH_3C(ONa)(OCOCH_3)_2$. The conversion of calcium acetate at higher temperatures into calcium carbonate can, obviously, also be understood on an analogous basis. Similarly, the constitution of the abnormal acid salts of potassium acetate and of potassium oxalate may be interpreted from this standpoint, *e. g.*, the very stable salt, $KOCOCH_3.HOOCCH_3$, being $CH_3C(OH)(OCOCH_3)OK$, etc.

The Dissociation of Sodium Benzylate.—The sodium benzylate used in all my experiments was prepared from fine sodium wire suspended in 25 parts of absolute ether, by addition of the calculated amount of benzyl alcohol and heating until all the metal disappeared. The ether was then removed by distillation in a stream of dry hydrogen and the salt remaining was, finally, heated in a bath raised to 180°.

Fifty grams of sodium benzylate were heated in a distilling flask connected, successively, with a condenser, a receiver, and an azotometer. As soon as the temperature of the surrounding bath reached 200° the salt began to melt and at 240° the molten mass began to decompose rapidly, with formation of gaseous and volatile liquid products. The temperature of the bath rose, finally, after 9 hours' heating, to 305°. By this time the gas evolution had practically ceased and the material in the distilling flask had entirely solidified and was colored yellow.

Four and five-tenths grams of mobile oil had collected in the receiver and the total amount of gas obtained was 3255 cc. Duplicate analyses of the later portion of the gas by Hempel's methods proved that it consisted mainly of hydrogen: Hydrocarbons, 1.4 per cent; carbon monoxide, 0.4 per cent; hydrogen, 91.5 per cent; oxygen, 1 per cent; and nitrogen, 5.7 per cent. The hydrocarbons were determined by absorption with alcohol; the hydrogen was determined in one case by absorption with palladium and in the other by explosion with air.

The 4.5 grams of oil in the receiver were found, by fractionation, to consist mainly of toluene, 3.3 grams boiling at 85°–115° and containing, therefore, small amounts of benzene; in addition, 1.2 grams of benzyl alcohol, boiling at 200°–201°, were obtained.

On adding 400 cc. of water to the residue left in the distilling flask, extracting with ether, etc., much neutral oil was obtained. This, upon fractionation under reduced pressure, gave 4.2 grams of benzyl alcohol, 1.5 grams of dibenzyl and 3 grams of non-volatile tar. The dibenzyl was purified by crystallization from ether and obtained in plates, melting unchanged at 51° when mixed with a known preparation of the substance.

Steam was now passed through the aqueous alkaline solution and, on cooling, an insoluble substance crystallized out, which, on recrystallization from alcohol, melted at 134° and weighed 1.4 grams. It was identified as benzoin by conversion into the β-phenylhydrazone of Smith and Ransom, m. p. 106°.[1]

On acidifying the alkaline solution with sulphuric acid no trace of carbon dioxide was obtained; the aqueous solution, on extracting with ether, etc., gave a total of 21.5 grams of crystalline residue. Only a portion of this dissolved in sodium carbonate, giving, finally, 9.2 grams of benzoic acid, m. p.

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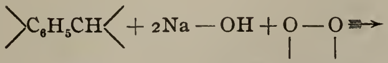
[1] THIS JOURNAL, 16, 112.

121°; the remainder consisted of a yellowish tar, neutral to sodium carbonate but soluble in caustic alkalies.

The formation of most of these products can readily be understood on the basis of Nef's work.[1] The main reaction is evidently conversion into benzoic acid and hydrogen, according to Dumas and Stas, a reaction which takes place quantitatively when benzyl alcohol is heated to 250° in the presence of an excess of potassium hydroxide or of soda lime.

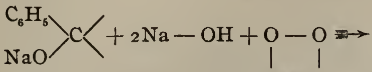
A portion of the phenylmethylene, formed by dissociation of the sodium benzylate, is reduced to toluene and to phenylmethyl, which polymerizes at once to dibenzyl. Part of the benzoic aldehyde, which is an intermediate product in the Dumas-Stas reaction, condenses to benzoin and another portion is split, to a very limited extent, into benzene and carbon monoxide. The regeneration of large amounts of benzyl alcohol indicates incomplete action or that water must have been formed in the reaction and, finally, the formation of large amounts of acid and neutral tars is due to the known tendency of phenylmethylene and of hydroxyphenylmethylene to form condensation products.

On the Oxidation of Sodium Benzylate in Dry Air.—According to Nef's interpretation of combustion phenomena,[1] the following reactions between the dissociated sodium benzylate molecules and the active oxygen molecules in the air must take place at considerable speed on passing dry air and oxygen over this salt at ordinary temperatures:

(I) 

$$>C_6H_5CH< + 2Na-OH + \underset{|}{O}-\underset{|}{O} \rightarrow$$

$$C_6H_5CH(OH)_2 + NaO.ONa \rightarrow C_6H_5CHO + H_2O + Na_2O_2;$$

(II) 

$$\begin{matrix} C_6H_5 \\ NaO \end{matrix}\!\!>C< + 2Na-OH + \underset{|}{O}-\underset{|}{O} \rightarrow$$

$$C_6H_5C(OH)_2ONa + NaO.ONa \rightarrow C_6H_5CO(ONa) + H_2O + Na_2O_2.$$

This was found to be the case. The water liberated, according to I. and II., sets free much benzyl alcohol which is, therefore, found unchanged at the end of the experiment. The sodium peroxide is, however, in great part used up in oxidizing the unchanged phenylmethylene and hydroxyphenylmethylene particles, so that only 1.4 per cent of the theoretical amount of Na_2O_2 was found at the end of the experiment. No trace of a peroxide,

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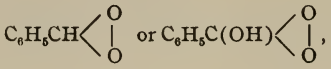
[1] Ann. Chem. (Liebig), 318, 173.

[2] *Ibid.*, 298, 294-301, 322-332; 318, 177-182.



$$C_6H_5CH{<}\begin{array}{c}O\\|\\O\end{array} \text{ or } C_6H_5C(OH){<}\begin{array}{c}O\\|\\O\end{array},$$

such as would be demanded by Engler and Bach's interpretation of combustion phenomena, was found in my experiments.

Dry air was slowly passed for 8 hours over 20 grams of sodium benzylate in a distilling flask, kept in a bath at 45°–55°. During the first 5 hours oxidation took place with noticeable evolution of heat. Finally, dry oxygen was passed over the mixture for 10 hours, at ordinary temperatures. On extracting the salt residue thoroughly with dry ether 5.7 grams of benzyl alcohol, b. p. 200°, were obtained. The salt residue, thoroughly dried, weighed 19.4 grams. By titration with standard thiosulphate, potassium iodide and sulphuric acid, the presence therein of 0.0838 gram of sodium peroxide was established.

Titration of another portion of the salt residue with normal sulphuric acid, using phenolphthalin as an indicator, proved that the total amount of sodium hydroxide present was 3.2 grams. Examination of a third portion proved that the total amount of benzoic acid present in the salt residue was 10.6 grams.

On the Behavior of Sodium Benzylate towards Benzyl Acetate, Ethyl Acetanilide, Formethylanilide, and towards Sodium Acetoaceticbenzyl Ester under Various Conditions.

On mixing sodium benzylate in a sealed tube with the dimolecular quantity of benzyl acetate, some heat evolution takes place and the mass gradually transforms itelf into a homogeneous, viscous condition. This mixture, whether allowed to stand for 25 days at 20° or heated for 50 hours at 100°, gives only a 2 per cent yield of acetoacetic benzyl ester, according to

$$2CH_3COOCH_2C_6H_5 + NaOCH_2C_6H_5 \rightleftarrows 2C_6H_5CH_2OH + CH_3C(ONa) : CHCOOCH_2C_6H_5.$$

This is in marked contrast to the corresponding reaction with ethyl acetate and sodium ethylate, where the equilibrium point is reached when about 36.5 per cent of sodium acetoacetic ester is formed.

Bacon has obtained entirely analogous results[1] in his experiments with benzhydrol acetate and sodium benzhydrol. Similarly, benzhydrol acetate and benzyl acetate, when treated directly or in absolute ether solution with metallic sodium, never give, under any condition yet found, more than about 1 per cent of the corresponding acetoacetic ester. In investigating the action of metallic sodium on benzyl acetate, Conrad and Hodgkinson found, to their surprise, some 25 years ago, that no trace of an acetoacetic benzyl ester is formed, whereas ethyl, butyl and amyl acetates, when treated with sodium, give relatively large yields of the corresponding acetoacetic ester. Conrad and Hodgkinson showed that mixtures of sodium and benzyl acetate remain unchanged until a temperature of 135° is reached, when suddenly a reaction takes place with violence and without hydrogen evolution, giving, among other products, benzyl hydrocinnamate.[2] Bacon has recently studied this reaction and proved that, in addition, much sodium benzylate and some dibenzyl oxide are formed.[3] It is obvious that the formation of benzyl hydrocinnamate is an alkylation phenomenon; the only point in doubt is whether this takes place through an intermediate formation of benzyl acetoacetate or whether it is due to a direct alkylation of the benzyl acetate by phenylmethylene, according to

$$C_6H_5CH< + H\text{—}CH_2COOCH_2C_6H_5 \rightleftarrows C_6H_5CH_2CH_2COOCH_2C_6H_5.$$

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[1] This Journal, **33**, 79–81.

[2] Ann. Chem. (Liebig), **193**, 298; **201**, 166.

[3] This Journal, **33**, 93–96.

Having investigated this question with especial care experimentally, I am led to the conclusion that here, as well as in the analogous experiments with benzyl propionate and butyrate, the alkylation must take place *directly*, *i. e.*, without intermediate formation of acetoacetic ester.

Copper Salt of Acetoacetic Benzyl Ester.—Shaklee has found[1] that acetoacetic benzyl ester is formed almost quantitatively by heating molecular proportions of benzyl alcohol and acetoacetic ester in a bath, at 160°. It is an oily liquid boiling, without decomposition, at 162°–164° (16 mm.). The ester boils with some decomposition at about 270° under ordinary pressure; it gives a blood-red coloration with ferric chloride and alcohol. Aqueous sodium hydroxide dissolves it in the cold without decomposition, whereas aqueous sodium carbonate is without effect. Treated in absolute ether solution with metallic sodium, in the form of wire, it is converted smoothly, with hydrogen evolution, into the sodium salt which separates as an insoluble, non-hygroscopic, white powder. The most characteristic derivative is the copper salt, which separates almost quantitatively as a green precipitate on adding an excess of aqueous copper acetate to an alcoholic solution of benzyl acetoacetic ester. On crystallizing the dry salt from benzene, green, feathery crystals, melting at 156°, are obtained.

0.1832 gram salt gave 0.0326 gram CuO.

0.2310 gram salt gave 0.0410 gram CuO.

0.1248 gram salt gave 0.2698 gram CO_2 and 0.0584 gram H_2O.

0.1476 gram salt gave 0.3196 gram CO_2 and 0.0637 gram H_2O.

	Calculated for $C_{22}H_{22}O_6Cu$.	Found.	
		I.	II.
Cu	14.27	14.21	14.18
C	59.24	58.95	59.05
H	4.94	5.19	4.79

Sodium Benzylate and Benzyl Acetate.—Twenty grams of sodium benzylate and 46.1 grams (2 mols.) of benzyl acetate, b. p. 210°–213°, were mixed and allowed to stand at ordinary temperatures, for 25 days, in a sealed tube. Union to form a viscous, homogeneous mass took place very soon, as mentioned above. On treating with an excess of dilute sulphuric acid much oil separated, which was taken up in ether and resolved, by further treatment with aqueous sodium carbonate, into neutral and acid products; 1.7 grams of benzoic acid and 0.8 gram of tar, insoluble in boiling water, were obtained from the soda solution.

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[1] THIS JOURNAL, 33, 80.

The neutral products were at first fractionated under reduced pressure; 43 grams of benzyl alcohol, containing some benzyl acetate and boiling at 200° to 210°, were obtained; in addition 4.8 grams of oil boiling at 130°–165° (20 mm.) and 2.8 grams of non-volatile tar were found. This high-boiling oil gave a strong ferric chloride reaction, and was, accordingly, treated, in alcoholic solution, with aqueous copper acetate. The precipitate obtained was crystallized from benzene, giving thus 0.6 gram of copper acetoacetic benzyl ester melting at 153°–154°.

0.2151 gram salt gave 0.0382 gram CuO.

	Calculated for $C_{22}H_{22}O_6Cu$.	Found.
Cu	14.27	14.18

A second experiment was carried out in which the same amount of material was heated in a sealed tube, at 100°, for 50 hours, 7 hours daily. The result was practically the same as in the first case; 0.6 gram of copper acetoacetic benzyl ester, melting at 156°, was obtained.

0.4820 gram salt gave 0.0852 gram CuO.

	Calculated for $C_{22}H_{22}O_6Cu$.	Found.
Cu	14.27	14.12

A third experiment, with 20 grams of sodium benzylate and 46.1 grams of benzyl acetate, heated in a sealed tube for 23 hours at 120°–130° and then for 9 hours at 130°–140°, gave the following result: A larger amount of neutral, high-boiling oil was obtained than in the former experiments, but no trace of benzyl acetoacetate could be detected therein by the ferric chloride reaction, by the formation of a copper salt, or by treatment with cold, aqueous sodium hydroxide. Special experiments, described below, show that sodium acetoacetic benzyl ester is decomposed by sodium benzylate even at 100° to a very large extent into its components and completely from 120° upwards. This result, taken in connection with the observation that mixtures of sodium benzylate and benzyl acetate under no conditions yet ascertained, give more than a 2 per cent yield of sodium acetoacetic benzyl ester, makes it certain that the formation of benzyl hydrocinnamate in my own and in Conrad and Hodgkinson's experiments must be due to a direct alkylation of benzyl acetate by phenylmethylene. The formation of benzyl hydrocinnamate or of hydrocinnamic acid from mixtures of benzyl acetate or of sodium acetoacetic benzyl ester and sodium benzylate begins noticeably at 100°, and increases rapidly in amount as the temperature is raised to 160°, whereas all traces of sodium acetoacetic benzyl ester disappear from 120° upwards.

Thus a fourth experiment with 20 grams of sodium benzylate and 23 grams of benzyl acetate (1 mol.) gave, after heating in a sealed tube, at 140°–160°, for 42 hours, 7 hours daily, the following result:

The main reaction products, neutral to sodium carbonate, fractionated under 20 mm. pressure, gave 1 gram of non-volatile tar, 19 grams of benzyl alcohol, b. p. 100°–115°, and 3.1 grams of oil boiling at 160°–200°. The high-boiling oil was shown by the usual tests to be entirely free from benzyl acetoacetate. It probably consisted of a mixture of dibenzyl oxide and of benzyl hydrocinnamate.[1] On working up the acid products, *i. e.*, those soluble in sodium carbonate, by acidifying, extracting with ether and fractionating under 25 mm. pressure, 6.5 grams of crystalline material, boiling at 100°–195°, were obtained. A heavy oil, 1.8 grams, remained in the distilling flask.

The 6.5 grams of volatile acids were separated by fractional crystallization from water into 3.1 grams of hydrocinnamic acid, m. p. 48°; 0.3 gram of cinnamic acid, m. p. 132°; and

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[1] Cf. Bacon: THIS JOURNAL, 33, 95–97.

0.4 gram of benzoic acid, m. p. 121°. This was proved in the first two cases by mixing portions with known preparations and finding that the melting point remained constant, as well as by the following analytical results:

0.4022 gram hydrocinnamic acid gave 1.0586 grams CO_2 and 0.2398 gram H_2O.

	Calculated for $C_9H_{10}O_2$.	Found.
C	72.00	71.78
H	6.66	6.62

0.1996 gram cinnamic acid gave 0.5304 gram CO_2 and 0.0982 gram H_2O.

	Calculated for $C_9H_8O_2$.	Found.
C	72.97	72.47
H	5.40	5.41

The cinnamic acid is undoubtedly formed by a condensation of benzoic aldehyde—obtained from sodium benzylate by the Dumas-Stas reaction, with benzyl acetate. The 1.8 grams of non-volatile oil, mentioned above,were found to consist chiefly of tar insoluble in hot water and on working up the portion soluble in boiling water 0.15 gram of dibenzylacetic acid, m. p. 87°, which was unchanged when mixed with a known preparation, was obtained.

Sodium Benzylate and Sodium Acetoacetic Benzyl Ester.—Fifteen grams of sodium acetoacetic benzyl ester and an equimolecular amount, 9.1 grams, of sodium benzylate, were intimately mixed in a mortar and then heated in a sealed tube, at 100°, for 100 hours, 10 hours daily. The tube was opened from time to time and some pressure, probably due to hydrogen, was noticed at first. On pouring into an excess of dilute sulphuric acid, separating into neutral and acid products, by means of sodium carbonate, etc., 6.6 grams of benzyl alcohol, b. p. 110°–150° (50 mm.),and 7.5 grams of oil, b. p. 150°–170° (20 mm.), were obtained. On treating the combined oils, in alcoholic solution, with aqueous copper acetate, 4 grams of copper acetoacetic benzyl ester, m. p. 156°, were obtained.

Only 0.5 gram of benzoic acid and no other acid could be found in the sodium carbonate solution.

A repetition of the experiment, using 15 grams of sodium acetoacetic benzyl ester and twice as much sodium benzylate, 18.2 grams, gave, after heating for 100 hours, at 100°, relatively more benzyl alcohol, 15 grams, and less high-boiling oil, 3.3 grams. The latter, however, contained only traces of acetoacetic benzyl ester and must, therefore, have consisted mainly of benzyl hydrocinnamate and dibenzyl oxide. This is also shown by the fact that on working up the sodium carbonate solution 0.5 gram of cinnamic acid, m. p. 132°, and 2 grams of hydrocinnamic acid, m. p. 48°, were obtained. In addition, some acetone was found in the original acidified aqueous solution after separating the insoluble oils.

In another experiment where an intimate mixture of 15 grams of sodium acetoacetic benzyl ester and 9.1 grams of sodium benzylate was heated in a sealed tube for 100 hours, 10 hours daily, at 150°–160°, 2 grams of pure hydrocinnamic acid and 0.7 gram of cinnamic acid were obtained. Finally, an experiment with 15 grams of sodium acetoacetic benzyl ester and 18.2 grams of sodium benzylate gave, after heating for 100 hours, at 150°–160°, etc., 7.5 grams of benzyl alcohol and 1 gram of high-boiling neutral oil, b. p. 120°–220° (25 mm.), which was found to be entirely free from acetoacetic ester. More acetone was found in this experiment than in the former ones. The sodium carbonate solution gave 0.4 gram of benzoic acid and 4.1 grams of pure hydrocinnamic acid, m. p. 48.

0.2308 gram hydrocinnamic acid gave 0.6098 gram CO_2 and 0.1368 gram H_2O.

	Calculated for $C_9H_{10}O_2$.	Found.
C	72.00	72.05
H	6.66	6.58

Finally, brief mention is made here of the fact that an intimate mixture of 33 grams of sodium benzylate and 41.6 grams of benzyl propionate gave, after heating in a sealed tube, for 100 hours, at 150°–160°, 1.8 grams of α-methylcinnamic acid, m. p. 79°.

0.1116 gram substance gave 0.3054 gram CO_2 and 0.0648 gram H_2O.

	Calculated for $C_{10}H_{10}O_2$.	Found.
C	74.74	74.63
H	6.17	6.35

Sodium Benzylate and Ethyl Acetanilide.—Twenty-four and nine-tenths grams of sodium benzylate (1.25 mols.) and 50 grams (2 mols.) of ethyl acetanilide, heated for a short time at 100°, in a sealed tube, were transformed into a homogeneous, viscous liquid and then heated 30 hours longer at that temperature. On pouring into an excess of dilute sulphuric acid and working up as is usual, for basic, acid and neutral products, 25 grams of ethyl aniline were obtained. The neutral portion gave, on fractionation (20 mm.), 10 grams of benzyl alcohol, b. p. 103°–105°, 2 grams of unchanged ethyl acetanilide, b. p. 145°–148°, and 14.1 grams of a heavy oil, boiling at 170°–210°, whose nature was not determined but which was obviously a mixture of dibenzyl oxide and benzyl hydrocinnamate. The portion soluble in aqueous sodium hydroxide contained 1.2 grams of acetic acid and 1.5 grams of acetoacetic benzyl ester, b. p. 150°–164° (20 mm.). The last-named substance gave, on treatment with aqueous copper acetate, etc., 0.4 gram of copper acetoacetic benzyl ester, m. p. 153°.

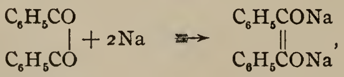
0.2648 gram substance gave 0.0462 gram CuO.

	Calculated for $C_{22}H_{22}O_6Cu$.	Found.
Cu	14.27	13.94

In a second experiment, where 20 grams of ethyl acetanilide and the monomolecular amount, 17 grams, of sodium benzylate were used, and the mixture was heated in a sealed tube for 44 hours, at 130°–150°, 13 grams of ethyl aniline and 7 grams of benzyl alcohol, b. p. 108°–110° (22 mm.), were obtained. The sodium carbonate solution contained 5.5 grams of acids boiling at 100°–170° (20 mm.). This was separated in the usual manner, giving 3 grams of hydrocinnamic acid and 0.5 gram of cinnamic acid.

Finally, brief mention is made here of 2 experiments with equimolecular quantities of sodium benzylate and ethyl formanilide (18 grams). In the first instance the mixture was heated in sealed tubes, for 43 hours, at 130°–150°, and in the second for 70 hours, at 150°–160°. Much benzoic acid was obtained, especially in the second experiment, but no benzylformic, *i. e.*, phenylacetic acid could be detected in either case.

On the Action of Metallic Sodium on Alkyl Acetates.—The observation that ethyl acetate, when diluted with absolute ether, reacts with metallic sodium without formation of hydrogen or sodium acetoacetic ether was first made 3 years ago in this laboratory by Bacon[1] at Dr. Nef's suggestion. Shaklee[1] had previously, under similar conditions, found that benzyl acetate and benzhydrol acetate, when diluted with absolute ether, react in the cold with metallic sodium and give mainly sodium benzylate and sodium benzhydrol, respectively. Only traces of hydrogen and of an acetoacetic ester derivative could be obtained, and in both cases the presence of a substance which gave the diacetylosazone of Pechmann, m. p. 242°, on treatment with phenylhydrazine acetate, was definitely established by Shaklee. He concluded, therefore, that diacetyl was formed in this reaction. Dimethyl ketol, however, can give the same compound on treatment with this reagent, and since Nef[2] has shown that benzil reacts with sodium according to



$$\begin{array}{r} C_6H_5CO \\ | \\ C_6H_5CO \end{array} + 2Na \longrightarrow \begin{array}{c} C_6H_5CONa \\ \| \\ C_6H_5CONa \end{array},$$

giving dinatroxystilbene, which is at once decomposed by water into benzoin and 2 molecules of sodium hydroxide, it was quite possible that the diacetyl first formed in the reaction might have been converted in an analogous manner, by more sodium, into dinatroxy-β-butylene, $CH_3C(ONa) : C(ONa)CH_3$, which must then give, with water, dimethyl ketol. It was possible, therefore, that dimethyl ketol and not diacetyl was the product formed in the reaction under discussion. This became practically certain when Bouveault and Locquin,[1] about a year ago, published the results of their work on the action of metallic sodum on ethyl butyrate and caproate. They found, for example, that sodium reacts with ethyl butyrate almost quantitatively, according to

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[1] THIS JOURNAL, 33, 77–79.

[2] Ann. Chem. (Liebig), 308, 287.

$$2C_3H_7C : O(OC_2H_5) + 4Na \rightarrow C_3H_7C(ONa) : C(ONa)C_3H_7 + 2C_2H_5ONa.$$

The product formed, dinatroxydipropylethylene, is at once decomposed by water, giving dipropyl ketol,

$$C_3H_7CH(OH)COC_3H_7.$$

It is clear from Nef's work[2] that the action of sodium on ethyl butyrate to give these end products must proceed through 5 successive stages. I now took up the study of the action of sodium on ethyl acetate in absolute ether solution and was able to confirm, in every detail, the previous observations of Bacon. When acetic ether is diluted with 7 parts of absolute ether and is then treated with metallic sodium, in wire form, not a trace of hydrogen or of sodium acetoacetic ester is formed; furthermore, exactly 2 atoms of sodium are used for every molecule of ethyl acetate taken, as demanded by the equation,

$$2CH_3COOC_2H_5 + 4Na \rightarrow CH_3C(ONa) : C(ONa)CH_3 + 2C_2H_5ONa.$$

The amount of sodium ethylate formed in the reaction was found to be exactly that demanded by the theory, but only small quantities of dimethyl ketol,

$$CH_3CH(OH)COCH_3,$$

or its monacetate, were actually obtained on treating the reaction products with dilute acids or with acetyl chloride. This is not surprising when one considers the well-known tendency of diacetyl, of acetol and of dimethyl ketol to undergo condensation, especially in the presence of caustic alkalies and of sodium alcoholates.

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[1] Compt. rend., **140**, 1593.

[2] Ann. Chem. (Liebig), **308**, 283–292; Cf. Acree: THIS JOURNAL, **29**, 588.

Thirty grams of sodium (2 atoms) in the form of wire were suspended in 500 cc. of absolute ether and 58 grams of pure ethyl acetate were added. A white coating appeared at once on the metal and in half an hour the temperature had risen 10°. Care was taken to keep the temperature below 34° and after an hour much light, brown powder appeared which continually increased in amount. At the end of 2 days the sodium was all gone; the calculated amount of 15 per cent hydrochloric acid was then added and the ethereal layer was well washed with water. The aqueous solution, when distilled under ordinary pressure, gave 30 grams of oil boiling at 78°–88° and 25 grams boiling at 88°–95°. These 2 fractions consisted mainly of alcohol and water, but both gave, on standing in the cold with aqueous phenylhydrazine acetate, diacetylosazone, m. p. 242°. The amounts were 3 grams and 1.8 grams, respectively. The ether solution, after getting rid of the ether by distillation, gave, on similar treatment, 0.7 gram more of pure diacetylosazone. The experiments described below with acetyl chloride prove that dimethyl ketol and not diacetyl is the reaction product under the conditions employed, and special experiments with pure dimethyl ketol and aqueous phenylhydrazine acetate have shown that only about 35 per cent of the theoretical amount of diacetylosazone can be obtained after 10 days' standing in the cold. From these data I conclude that the amount of dimethyl ketol formed from the 30 grams of sodium and 58 grams of ethyl acetate mentioned above must have been 4.14 grams.

Two experiments with sodium and the equimolecular amount of ethyl acetate were carried out in absolute ether solutions to prove that no trace of hydrogen is formed in the reaction. In the one case 26 grams of sodium, 88 grams of ethyl acetate and 1 liter of ether, in the other 19.6 grams of sodium, 75 grams of ethyl acetate and 700 cc. of ether were used. The flask containing the material was connected with a gasometer containing water. The amount of gas obtained was 1571 cc. and 991 cc., respectively. It was proved by analysis to contain no trace of hydrogen and was found to consist of a mixture of air and ether vapor. In a third experiment an extremely small amount of hydrogen was formed. These results are in entire accord with those of Bacon, who, in 5 experiments, using 176 grams of ethyl acetate and the monatomic quantity of sodium in every case, found that only traces of hydrogen and of acetoacetic ester had been formed.[1]

Estimation of the Sodium Ethylate Formed in the Reaction.—Twenty-six and one-tenth grams of sodium, 350 cc. of ether and 50 grams of ethyl acetate were allowed to stand until no more metal was present, and then 170 grams of freshly distilled benzoyl chloride were added and the mixture heated under a reversed condenser, in a bath kept at 45°–55°, for 7 hours. The oils left after filtering from the sodium chloride and distilling off the ether were fractionated (20 mm.) and the fraction boiling at 100°–120° was freed from benzoyl chloride by shaking with cold 25 per cent sodium hydroxide; 83.3 grams of ethyl benzoate, b. p. 210°, were thus finally obtained, which corresponds to 25.5 grams of ethyl alcohol. The amount demanded by the theory is 26.0 grams. It should be mentioned that after removing the benzoyl chloride and ethyl benzoate under reduced pressure, much non-volatile oil, 71 grams, remained in the distilling flask. This did not solidify, and judging from the corresponding experiments with acetyl chloride (see below), much dibenzoyloxy-β-butylene, as well as benzoyl derivatives of condensation products of diacetyl and of dimethyl ketol, may be present.

Action of Acetyl Chloride on the Mixture of Sodium Salts.—Twenty-six and one-tenth grams of sodium, suspended in the form of wire in 500 cc. of absolute ether, were treated with 50 grams of ethyl acetate. When the metal had disappeared, 95 grams of freshly distilled acetyl chloride were added slowly, taking care to shake well and to cool with running water. The mixture was allowed to stand 2 hours, water was then added and the ethereal solution well washed with aqueous sodium carbonate and then dried with calcium chloride. The ether was distilled off by means of a Glinsky apparatus and the oil remaining then fractionated under reduced pressure. The first distillation gave the following fractions:

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[1] THIS JOURNAL, 33, 79.

I. 5.8 grams, boiling at 45°–60° (30 mm.).
II. 5.5 grams, boiling at 60°–90° (20 mm.).
III. 7.8 grams, boiling at 90°–110° (18 mm.).
IV. 11.3 grams, boiling at 110°–140° (18 mm.).

Twelve grams of non-volatile, tarry oil remained in the distilling flask. It was found impossible, by further fractionation, to obtain constant boiling products; furthermore, much loss occurs in every subsequent distillation through condensation. Fraction I. was proved to consist mainly of dimethyl ketol and fraction II. of dimethyl ketol monacetate. Both of these fractions dissolve easily in water. Fractions III. and IV. are only very slightly soluble in water and give, on hydrolysis with water at 100°, acetic acid and dimethyl ketol; it is, therefore, very probable that much diacetyloxy-β-butylene, $CH_3C(OCOCH_3) : C(OCOCH_3)CH_3$, is present in these fractions.

All the fractions obtained, I.–IV., reduce Fehling's solution slowly in the cold, and rapidly on warming; treated with phenylhydrazine acetate they all give, on standing in the cold for 10 days, diacetylosazone, m. p. 242.

In order to have sufficient material for the experiments described in the following pages, more ethyl acetate was treated with sodium, acetyl chloride, etc., and the corresponding fractions obtained were then united. The result is the same whether the reaction products, after treatment with acetyl chloride, are worked up by filtration from the sodium chloride, *i. e.*, without contact with water, or by treatment with aqueous sodium carbonate. It was found necessary to prepare dimethyl ketol and also its monacetate in order to ascertain the best methods for identifying these substances. Dimethyl ketol[1] boils at 48°–50° (20 mm.); and the monacetate, which is readily made from dimethyl ketol and acetic anhydride, boils at 74° under the same pressure. Kling[1] states that dimethyl ketol gives a semicarbazone, m. p. 184°. I have found that space isomeric semicarbazones are formed in this case, which are difficult to separate, so that this is not a sharp method for identifying dimethyl ketol. On the other hand, dimethyl ketol monacetate gives, as I have found, a very characteristic semicarbazone. One gram of the acetate was added to a solution of 2 grams of semicarbazine hydrochloride in 5 cc. of water, previously treated with 1.3 grams of potassium carbonate. The semicarbazone separated at once as a bulky precipitate and on crystallization from 10 parts of hot water, 1.4 grams of the pure substance were obtained in white needles, melting at 162°.

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[1] The best method of preparing dimethylketol is that of Vladesco, Bull. Soc. Chim. [3] **6**, 407, 801, from methyl-α-chlorethyl ketone. Its preparation from the corresponding methyl-α-bromethyl ketone, which boils at 29°–30° (10 mm.), was found to be exceedingly tedious, owing to the difficulty of separation from the isomeric ethyl brommethyl ketone.

0.2517 gram substance gave 51.5 cc. N at 27° and 740 mm.

0.2212 gram substance gave 46 cc. N at 29° and 743 mm.

0.1643 gram substance gave 0.2673 gram CO_2 and 0.1050 gram H_2O.

	Calculated for $CH_3CHOCOCH_3$ | $CH_3C{:}NNHCONH_2$	Found. I.	 II.
C	44.86	44.34	....
H	7.00	7.15	....
N	22.49	22.69	22.70

The yield is quantitative. It was, therefore, possible to prove sharply, by means of the carbazone, that the fractions boiling at 70°–90° (20 mm.), and obtained from ethyl acetate, sodium and acetyl chloride, as described above, consist mainly of dimethyl ketol monacetate. Thus, 1.3 grams of oil, b. p. 88°–90° (30 mm.) gave, on treatment with semicarbazine, etc., 1.3 grams of semicarbazone of dimethyl ketol monacetate, melting, after one crystallization from water, at 158°.

I. 0.1823 gram substance gave 37 cc. N at 24° and 751 mm.

II. 0.1994 gram substance gave 40.5 cc. N at 26° and 751 mm.

	Calculated for $C_7H_{13}N_3O_3$.	Found. I.	 II.
N	22.49	22.77	22.63

In another experiment, where 7 grams of oil, b. p. 45°–70°

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[1] Ann. Chim. Phys. [8], 5, 552.

(25 mm.), were heated for 18 hours, at 100°, with 10 grams of acetic anhydride and the mixture was then treated with water, extracted with ether and dried with potassium carbonate, 1.5 grams of dimethyl ketol monacetate, boiling at 73°–74° (17 mm.), were obtained. This gave 0.8 gram of semicarbazone, m. p. 162°.

0.2386 gram substance gave 48.5 cc. N at 27° and 753 mm.

	Calculated for $C_7H_{13}N_3O_3$.	Found.
N	22.49	22.87

On treating the higher boiling oils, 90°–140° (20 mm.), obtained in the reaction under consideration, with 3 parts of water in sealed tubes, for 25 hours, at 100°, they are all decomposed, giving acetic acid and dimethyl ketol. The amount of acetic acid formed was determined by treating the resulting aqueous solutions with powdered calcium carbonate and determining the amount of unaffected carbonate, as well as by weighing the calcium acetate left after distilling off the water and dimethyl ketol on a boiling water-bath (20 mm.). The amount of acetic acid found was invariably small, *i. e.*, far less than that demanded for the hydrolysis of a substance like $CH_3C(OCOCH_3),: C(OCOCH_3)CH_3$, for instance, but the amount of dimethyl ketol obtained in the aqueous distillate was also correspondingly small, so that one must conclude that only small amounts of diacetyldihydroxy-β-butylene can be present in the oils boiling at 90° to 140° (20 mm.); the nature of the main products present remains, therefore, undetermined.

Thus, 14.5 grams of oil boiling at 80°-120° (20 mm.), heated for 35 hours at 100°, with 45 grams of water, used up 3.55 grams of calcium carbonate and gave 6.2 grams of calcium acetate, $Ca(C_2H_3O_2)_2.H_2O$.

Four and one-tenth grams of oil, boiling at 80° to 95° (12 mm.), heated with 13 grams of water, in a sealed tube, for 25 hours, at 100°, used up 1.2 grams of calcium carbonate and gave 2.08 grams of calcium acetate. The aqueous distillate was, in this case, extracted 20 times with ether; after drying and then distilling off the ether by means of a Glinsky apparatus, the oil remaining gave, on standing for 7 days with aqueous phenylhydrazine acetate, 0.55 gram diacetylosazone, m. p. 242°.

Finally, the following experiments with various non-hydrolyzed fractions obtained in the reaction under consideration are of interest.

One gram of oil boiling at 40°–45° (40 mm.) gave, on standing in the cold for 1 week with aqueous phenylhydrazine acetate, 0.35 gram of pure diacetylosazone. One gram of oil boiling at 45° to 70° (38 mm.) gave, on similar treatment, 1.05 grams of osazone. One gram of oil, boiling at 57° to 60° (20 mm.), gave 1.2 grams of osazone. The diacetylosazones obtained in these 3 cases were simply filtered off and washed with cold ether; they all melted constantly at 242°.

0.2681 gram substance gave 51 cc. N at 27° and 752 mm.

	Calculated for $C_{16}H_{18}N_4$.	Found.
N	21.08	21.16

One gram of oil boiling at 95° to 104° (14 mm.) gave, on similar treatment with aqueous phenylhydrazine acetate, 0.5 gram of osazone. Another fraction, one gram of oil boiling at 105° to 115° (14 mm.), gave 0.4 gram of diacetyl osazone, m. p. 242°.

0.2856 gram substance gave 54.65 cc. N at 27° and 749 mm.

	Calculated for $C_{16}H_{18}N_4$.	Found.
N	21.08	21.20

The results presented above prove decisively, therefore, that small quantities of dimethyl ketol are formed by the action of sodium on ethyl acetate when diluted with absolute ether. The major portion of the dimethyl ketol, as well as of the diacetyl, which is obviously an intermediate product in the reaction, must at once undergo further condensation. This is not surprising, in view of the well-known properties of these compounds. Finally, mention should be made of an experiment where 13.4 grams (diatomic quantity) of sodium, suspended in the form of wire in 250 cc. of absolute ether, were treated with 25 grams of diacetyl, b. p. 87°–91°. Action took place slowly and without hydrogen evolution. The metal gradually crumbled and a reddish-brown powder took its place. At the end of one week no further action was noticeable and about one-half of the sodium remained unchanged.[1] The mixture was now treated with 35 grams of acetyl chloride, and after 2 hours' standing, was worked up by filtering from the sodium chloride and the sodium and then distilling off the ether by means of a Glinsky apparatus. On attempting to distil the oil left, 30 grams, practically nothing distilled off (25 mm.) even when the temperature of the surrounding bath had reached 200°; 27 grams of dark, viscous tar remained in the distilling flask.

In conclusion, I wish to express my thanks to Professor Nef for the inspiration and help which he has given me in this work.

THE OSMOTIC PRESSURE AND THE DEPRESSION OF THE FREEZING POINTS OF SOLUTIONS OF GLUCOSE.[2]

By H. N. Morse, J. C. W. Frazer, and B. F. Lovelace.

PART II.

In Part I. of this paper[3] we described the measures which had been taken to secure uniform temperatures in the bath in which the osmotic cell is located during an experiment, also certain improvements in apparatus and modifications of procedure which had been introduced since the earlier work[4] upon the osmotic pressure of cane sugar. We also described a difficulty encountered early in the work, which was due to the persistent infection of the cells with *penicillium*; and the efforts which were made to find an efficient poison for the fungus which could be employed without injury to the membranes and without sensible effect upon the accuracy of the results.

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[1] Cf. corresponding experiment of Nef with benzil, Ann. Chem. (Liebig), 308, 286–7.

[2] The work upon osmotic pressure which is in progress in this laboratory is aided by grants from the Carnegie Institution.

[3] This Journal, 36, 1.

[4] *Ibid.*, 34, 1.

In this part of the paper the formal measurements will be presented with only such additional matter as may be necessary to an understanding of the conditions under which they were made.

It was stated[1] that the difficulty of preparing non-permeable membranes increases as the molecular weights of the substances diminish, and that a membrane which is not sensibly permeable to cane sugar may leak glucose. Except in one instance, only two cells, "A" and "D," were employed for the present measurements because, of the half dozen cells now in use, they were the most readily brought into fit condition[2] for the work. "A" has been long in service[3] and had developed such slowness in reaching maximum pressures that it was subjected early in the work to a process of renovation. This "renovation" is resorted to whenever the wall of a cell becomes so filled with membrane material that the passage of water through it is intolerably slow, and also when there is reason to suspect that the junction[4] between the glass tube and the soapstone ring, or that between the ring and the cell wall, has become defective. The process consists in opening the cell by digging out the cement, and in removing the membrane by soaking the cell successively in a warm solution of an alkaline tartrate, in water, in hydrochloric acid, and finally again in water. To remove any soluble matter still remaining in the wall, the cell is placed in dilute hydrochloric acid, which is electrolyzed with the cell wall between the poles. The acid is replaced by water—with frequent renewals of the latter—and the electrolysis is continued until the conductivity is reduced to about that of the distilled water. Finally, the cell is reburned at a temperature of 900° or 1000° and is thereafter treated in every respect like a new cell[5].

In A, solutions of all concentrations developed their maximum pressures continuously and maintained them for long periods, showing that the membrane did not leak. The conduct of D, in this respect, was also satisfactory except in one or two instances, where, after having reached a maximum, the pressure exhibited a slight tendency to decline, suggesting either that the membranes, on those occasions, were not wholly impervious to the glucose, or that some of the joints of the cell had become slightly defective. D was accordingly withdrawn for "renovation" and the work was finished with A. The cell G, which was employed for a single measurement (Table XVI.), likewise exhibited an inability to maintain a maximum pressure for a long period, and it was withdrawn for renovation and for subsequent use in the measurement of the pressure of cane sugar solutions at 0°.

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[1] THIS JOURNAL, **36**, 33.
[2] *Ibid.*, **36**, 30.
[3] *Ibid.*, **36**, 54.
[4] *Ibid.*, **34**, 11.
[5] *Ibid.*, **34**, 11; **36**, 30.

The preparation of the manometers has been described in sufficient detail elsewhere,[1] and the only additional fact concerning them which should be recorded here relates to the possible gradual reduction of the air volumes through the action of the oxygen on the impurities in the mercury. To prepare the mercury for manometric purposes, it was sprayed daily for 3 weeks, according to the method of Lothar Meyer, through 1.75 meter columns of solutions of ferric chloride, hydrochloric acid, and nitric acid, and then preserved under concentrated sulphuric acid. Notwithstanding this thorough treatment of the mercury, the air volumes in our manometers have sensibly diminished in the course of time, especially in those which have been frequently used for the measurement of the higher pressures. According to the last verifications the diminution in the manometers most frequently employed in the present work (numbers 5, 6, 11, and 13) has amounted respectively to 1.66, 1.29, 1.68, and 1.80 per cent of the original air volumes. It is hardly necessary to state that appropriate corrections have been applied for this diminution of the air volumes. In the future, the mercury which is to be used in manometers will be prepared from the pure oxide and the instruments will be filled with nitrogen instead of air.

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[1] THIS JOURNAL, 34, 3; 36, 20.

It was stated in Part I. of this paper[1] that an effective remedy for *penicillium* had been found in extremely dilute solutions of thymol, also that the same solutions retarded, in a marked degree, the alcoholic fermentation which must be carefully guarded against in all experiments with glucose. Hence all liquids used in the present work—the sugar solutions, the liquid in which the cells are immersed during an experiment, and the water in which they are soaked at all times when not in use—have been made 0.001 weight-normal with respect to thymol. There has been no reappearance of *penicillium*, nor have we observed at any time any indication of alcoholic fermentation in the solutions of glucose.

In the tables which follow, the rotation (in saccharimeter degrees) of the solution, before and after a measurement, is given. It will be noticed that in all cases, except two, the rotation was less at the close of an experiment than in the beginning, indicating a dilution of the solution while in the cell, and that a correction has been made for this dilution in each case. The causes of the observed dilution of the solutions while in the cells have been amply discussed in former papers[2] but the importance of the subject justifies a re-enumeration of them. They are, (1) the distension of the cell under pressure; (2) the entrance into the manometer of a volume of the liquid equal to the diminution of the air volume; (3) the pushing upwards of the manometer through the stopper; (4) the upward displacement of the material of the stopper; (5) the sucking in of water from the cell wall by the solution while the cell is being closed at the beginning, and opened at the end of an experiment; (6) fermentation (which would cause a loss of rotation); and, finally, (7) leakage of the membrane.

The ability of the membranes employed in this work to maintain *maximum* pressures for long periods was demonstrated before the formal measurements here recorded were undertaken, and whenever a cell showed itself at all defective in this respect it was withdrawn.

The more important sources of dilution of the cell contents are to be looked for among the causes enumerated under 3, 4 and 5, namely, the pushing, upward of the manometer, the upward displacement of the material of the stopper, and the sucking in of water from the cell wall. Of the three, the last is believed to have had the greatest effect in bringing about a dilution of the glucose solutions while in the cells.

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[1] THIS JOURNAL, **36**, 34.

[2] *Ibid.*, **36**, 26, 48.

The amount of dilution due to distortion of the stopper and the sucking in of water cannot be ascertained, but that due to upward displacement of the manometer is easily calculated. The following table—giving the results of a few such calculations—will show that it is not, as a rule, the principal cause of dilution:

Table I.

Weight-normal concentration.	Number of experiment.	Upward displacement of manometer. mm.	Amount of dilution. Percentage.	Dilution due to displacement of manometer. Percentage.
0.3	2	0.52	0.64	0.07
0.5	2	0.57	1.16	0.08
0.6	1	7.29	3.76	0.94
"	3	0.76	0.32	0.11
0.7	2	3.24	2.82	0.21
"	3	6.11	1.69	0.84
0.8	1	9.82	2.76	1.42
"	2	2.11	1.74	0.30
"	3	2.12	1.74	0.30
0.9	1	2.57	1.45	0.35
"	2	0.98	1.00	0.12
"	3	1.69	0.66	0.23
1.0	1	1.49	0.91	0.20
"	2	1.56	0.91	0.14
"	3	1.24	1.72	0.17

When all loss of rotation in the contents of the cell is ascribable to *dilution*, as in the case of glucose, the difficulty is not a serious one; but when, as in the case of cane sugar, it is due partly to *dilution* and partly to *inversion*, it becomes highly important to eliminate, or at least to reduce to insignificance, the dilution factor. With this end in view, we have in process of construction a new form of cell which, it is hoped, will enable us to dispense with rubber stoppers and which can be much more expeditiously closed and opened than the cells we are now using.

The material of which the glucose solutions were made is that known as "*Traubenzucker Kahlbaum.*" It was pulverized, placed over calcium chloride and freely aerated by means of a current of dried air in order to hasten the removal of the odor of alcohol. After this treatment the material did not sensibly lose in weight when heated to a higher temperature in an air-bath. It melted quite sharply at 146°. Two determinations of carbon and hydrogen gave 40.03 and 40.04, instead of 39.98 per cent for the former, and 6.84 and 6.83 instead of 6.71 per cent for the latter.

The more important details of the individual measurements which are contained in Tables II. to XXVI., inclusive, are brought together in Table XXVII., which gives for each experiment: (1) the temperatures of the bath-mean, highest, and lowest; (2) the observed osmotic pressure-mean, highest, and lowest; (3) the calculated pressure-mean, highest, and lowest, if molecular-equivalent quantities of a gas are confined within the volume of the solvent at the same temperatures; (4) the differences, expressed in fractions of an atmosphere, between the mean osmotic and the mean calculated gas pressure; (5) the molecular weight of glucose—mean, highest and lowest—calculated from the observed osmotic pressures; and, finally, (6) the mean molecular weights for each concentration.

Table XXVIII. contains only the mean temperatures, the mean osmotic and the calculated gas pressures and their differences, and the mean calculated molecular weights.

A general view of the results is most readily obtained by an inspection of Table XXVIII., while an independent judgment of the weight to be attached to any individual determination can be arrived at by tracing it backwards through Table XXVII. to that in which the details of the measurement are given.

In order to facilitate a comparison of the results for glucose with those earlier obtained for cane sugar, two other tables (Nos. XXIX. and XXX.) have been introduced. They

Table II.

Original wt. normal concentration of solution, 0.1.
Rotation of original solution, $5^\circ.4$.
Rotation at conclusion of experiment, $5^\circ.2$.
Percentage loss in concentration, 3.70 per cent.
Calibration units of air in manometer, 473.77.
Time of setting up cell, 4.30 P.M., April 18, 1906.

Experiment No. 1.
Manometer used, No. 11.
Capillary depression, 0.02 atmosphere.
Cell used, D.
Resistance of membrane, 65,000 ohms.
Initial pressure.

Time.	Temperature.		Volume of air in manometer.		Corrections.							
	Solution.	Air in manometer.	Uncorrected.	Corrected.	Atmospheric pressure.	Liquids in manometer.	Dilution of cell contents.	Capillary depression.	Osmotic pressure corrected.	Theoretical gas pressure.	Difference between pressure found and calculated.	Mol. Wt. calculated from osmotic pressure.
April 19												
11.00 A.M.	$23^\circ.5$	$22^\circ.8$	185.28									
2.00 P.M.	$23^\circ.5$	$23^\circ.1$	185.08									
4.30 P.M.	$23^\circ.5$	$23^\circ.4$	185.03									
April 20												
9.00 A.M.	$23^\circ.6$	$23^\circ.4$	185.06									
5.30 P.M.	$23^\circ.7$	$24^\circ.5$	184.70									
April 21												
11.00 A.M.	$24^\circ.0$	$24^\circ.5$	181.46									
3.00 P.M.	$24^\circ.1$	$24^\circ.6$	181.00	166.01	0.99	0.36	0.09	0.02	2.33	2.42	—0.09	
April 22												
11.00 A.M.	$24^\circ.3$	$24^\circ.1$	179.01	164.46	0.99	0.36	0.09	0.02	2.36	2.43	—0.07	
6.00 P.M.	$24^\circ.4$	$23^\circ.9$	178.77	164.35	0.99	0.36	0.09	0.02	2.37	2.43	—0.06	
April 23												
4.00 P.M.	$24^\circ.1$	$22^\circ.8$	177.48	163.77	0.99	0.36	0.09	0.02	2.38	2.42	—0.04	182.0
April 24												
10.00 A.M.	$23^\circ.9$	$23^\circ.4$	176.42	162.46	0.99	0.36	0.09	0.02	2.39	2.42	—0.03	181.1
3.00 P.M.	$23^\circ.9$	$23^\circ.5$	176.46	162.45	0.99	0.36	0.09	0.02	2.39	2.42	—0.03	181.1

H = 1 Mol. Wt. Glucose = 178.74 Mean Mol. Wt. 181.4

Table III.

Original wt. normal concentration of solution, 0.1.
Rotation of original solution, 5°.4.
Rotation at conclusion of experiment, 5°.4.
Percentage loss in concentration, 0.0 per cent.
Calibration units of air in manometer, 442.92.
Time of setting up cell, 12.00 M., May 29, 1906.

Experiment No. 2.
Manometer used, No. 13.
Capillary depression, 0.02 atmosphere.
Cell used, D.
Resistance of membrane, 115,000 ohms.
Initial pressure, 1.9 atmospheres.

	Temperature.		Volume of air in manometer.		Corrections.							
Time.	Solution.	Air in manometer.	Uncorrected.	Corrected.	Atmospheric pressure.	Liquids in manometer.	Dilution of cell contents.	Capillary depression.	Osmotic pressure corrected.	Theoretical gas pressure.	Difference between pressure found and calculated.	Mol. Wt. calculated from osmotic pressure.
May 29												
2.30 P.M.	25°.6	24°.7	153.67									
4.45 P.M.	25°.6	24°.8	154.92									
May 30												
9.30 A.M.	25°.4	24°.4	159.60									
4.30 P.M.	25°.2	24°.6	162.46									
May 31												
10.00 A.M.	25°.1	24°.5	164.98	151.37	1.00	0.47	0.00	0.02	2.41	2.43	—0.02	180.3
5.30 P.M.	25°.0	25°.5	165.44	151.28	1.00	0.47	0.00	0.02	2.42	2.43	—0.01	179.5
June 1												
10.00 A.M.	25°.2	25°.1	165.22	151.28	1.00	0.47	0.00	0.02	2.42	2.43	—0.01	179.7

H = 1 Mol. Wt. Glucose = 178.74 Mean Mol. Wt. 179.83

Table IV.

Original wt. normal concentration of solution, 0.2.
Rotation of original solution, 10°.6.
Rotation at conclusion of experiment, 10°.5.
Percentage loss in concentration, 0.94 per cent.
Calibration units of air in manometer, 441.97.
Time of setting up cell, 5.00 P.M., April 26, 1906.

Experiment No. 1.
Manometer used, No. 8.
Capillary depression, 0.02 atmosphere.
Cell used, D.
Resistance of membrane, 94,000 ohms.
Initial pressure.

Time.	Temperature.		Volume of air in manometer.		Corrections.				Osmotic pressure corrected.	Theoretical gas pressure.	Difference between pressure found and calculated.	Mol. Wt. calculated from osmotic pressure.
	Solution.	Air in manometer.	Uncorrected.	Corrected.	Atmospheric pressure.	Liquids in manometer.	Dilution of cell contents.	Capillary depression.				
April 27 11.00 A.M.	22°.9	23°.2	94.18									
4.00 P.M.	22°.9	23°.7	94.42									
April 28 11.00 A.M.	23°.3	24°.1	94.77									
April 29 10.00 A.M.	23°.6	23°.3	94.74									
April 30 10.00 A.M.	23°.6	24°.1	94.79									
5.00 P.M.	23°.7	24°.1	94.70									
May 1 9.00 A.M.	24°.0	24°.3	94.44	86.71	1.00	0.59	0.05	0.02	4.75	4.85	—0.10	182.3
3.00 P.M.	24°.0	24°.1	94.42	86.74	1.00	0.59	0.05	0.02	4.75	4.85	—0.10	182.3
May 2 11.00 A.M.	24°.2	24°.3	94.36	86.63	0.99	0.59	0.05	0.02	4.79	4.85	—0.06	180.7

H = 1 Mol. Wt. Glucose = 178.74 Mean Mol. Wt. 181.77

Table V.

Original wt. normal concentration of solution, 0.2.
Rotation of original solution, 10°.6.
Rotation at conclusion of experiment, 10°.5.
Percentage loss in concentration, 0.94 per cent.
Calibration units of air in manometer, 473.77.
Time of setting up cell, 4.15 P.M., May 3, 1906.

Experiment No. 2.
Manometer used, No. 11.
Capillary depression, 0.02 atmosphere.
Cell used, D.
Resistance of membrane, 91,000 ohms.
Initial pressure.

Time.	Temperature.		Volume of air in manometer.		Corrections.				Osmotic pressure corrected.	Theoretical gas pressure.	Difference between pressure found and calculated.	Mol. Wt. calculated from osmotic pressure.
	Solution.	Air in manometer.	Uncorrected.	Corrected.	Atmospheric pressure.	Liquids in manometer.	Dilution of cell contents.	Capillary depression.				
May 3 9.00 P.M.	24°.9	25°.4	100.89									
May 4 9.00 A.M.	24°.9	24°.7	98.73									
5.00 P.M.	24°.9	24°.9	99.18									
May 5 10.00 A.M.	25°.0	24°.9	99.32									
May 6 10.30 A.M.	25°.2	25°.3	99.17	90.74	0.99	0.47	0.05	0.02	4.77	4.86	—0.09	182.3
May 7 10.00 A.M.	25°.1	24°.3	98.90	90.80	1.00	0.47	0.05	0.02	4.76	4.86	—0.10	182.6
May 8 12.00 M.	24°.7	23°.9	98.43	90.49	1.00	0.47	0.05	0.02	4.77	4.86	—0.09	181.9
2.30 P.M.	24°.7	24°.1	98.43	90.43	1.00	0.47	0.05	0.02	4.78	4.86	—0.08	181.6

H = 1 Mol. Wt. Glucose = 178.74 Mean Mol. Wt. 182.10

Table VI.

Original wt. normal concentration of solution, 0.3.
Rotation of original solution, 15°.7.
Rotation at conclusion of experiment, 15°.7.
Percentage loss in concentration, 0.00 per cent.
Calibration units of air in manometer, 473.77.
Time of setting up cell, 4.15 P.M., May 10, 1906.

Experiment No. 1.
Manometer used, No. 11.
Capillary depression, 0.02 atmosphere.
Cell used, D.
Resistance of membrane, 108,000 ohms.
Initial pressure, 5.9 atmospheres.

Time.	Temperature.		Volume of air in manometer.		Corrections.				Osmotic pressure corrected.	Theoretical gas pressure.	Difference between pressure found and calculated.	Mol. Wt. calculated from osmotic pressure.
	Solution.	Air in manometer.	Uncorrected.	Corrected.	Atmospheric pressure.	Liquids in manometer.	Dilution of cell contents.	Capillary depression.				
May 11 11.00 A.M.	22°.2	21°.9	67.19	62.19	1.00	0.51	0.00	0.02	7.15	7.22	—0.07	180.5
2.30 P.M.	22°.2	22°.0	67.28	62.25	1.00	0.51	0.00	0.02	7.14	7.22	—0.08	180.8
5.00 P.M.	22°.3	22°.6	67.81	62.61	1.00	0.51	0.00	0.02	7.10	7.22	—0.12	181.9
May 12 10.00 A.M.	22°.2	22°.1	67.83	62.73	1.00	0.51	0.00	0.02	7.08	7.22	—0.14	182.3

H = 1 Mol. Wt. Glucose = 178.74

Mean Mol. Wt. 181.38

Table VII.

Original wt. normal concentration of solution, 0.3.
Rotation of original solution, 15°.7.
Rotation at conclusion of experiment, 15°.6.
Percentage loss in concentration, 0.64 per cent.
Calibration units of air in manometer, 473.77.
Time of setting up cell, 4.30 P.M., May 14, 1906.

Experiment No. 2.
Manometer used, No. 11.
Capillary depression, 0.02 atmosphere.
Cell used, D.
Resistance of membrane, 91,000 ohms.
Initial pressure, 5.9 atmospheres.

	Temperature.		Volume of air in manometer.		Corrections.							
Time.	Solution.	Air in manometer.	Uncorrected.	Corrected.	Atmospheric pressure.	Liquids in manometer.	Dilution of cell contents.	Capillary depression.	Osmotic pressure corrected.	Theoretical gas pressure.	Difference between pressure found and calculated.	Mol. Wt. calculated from osmotic pressure.
May 14 10.40 P.M.	23°.3	24°.8	68.65	62.92	1.01	0.51	0.05	0.02	7.10	7.25	—0.15	
May 15 9.00 A.M.	23°.5	24°.1	67.67	62.17	1.01	0.51	0.05	0.02	7.19	7.25	—0.06	180.3
2.30 P.M.	23°.5	23°.8	67.73	62.29	1.01	0.51	0.05	0.02	7.17	7.25	—0.08	180.8
May 16 3.30 P.M.	23°.6	23°.7	67.95	62.51	1.00	0.51	0.05	0.02	7.16	7.26	—0.10	181.1

Displacement of manometer = 0.52 mm.

Dilution due to displacement of manometer = 0.07 per cent. Mean Mol. Wt. 180.73

H = 1 Mol. Wt. Glucose = 178.74.

Table VIII.

Original wt. normal concentration of solution, 0.4.
Rotation of original solution, 20°.8.
Rotation at conclusion of experiment, 20°.7.
Percentage loss in concentration, 0.48 per cent.
Calibration units of air in manometer, 442.92.
Time of setting up cell, 4.30 P.M., May 22, 1906.

Experiment No. 1.
Manometer used, No. 13.
Capillary depression, 0.02 atmosphere.
Cell used, D.
Resistance of membrane, 97,000.
Initial pressure, 5.7 atmospheres.

Time. May 23	Temperature.		Volume of air in manometer.		Corrections.				Osmotic pressure corrected.	Theoretical gas pressure.	Difference between pressure found and calculated.	Mol. Wt. calculated from osmotic pressure.
	Solution.	Air in manometer.	Uncorrected.	Corrected.	Atmospheric pressure.	Liquids in manometer.	Dilution of cell contents.	Capillary depression.				
10.00 A.M.	27°.0	26°.1	48.28	44.06	1.01	0.61	0.05	0.02	9.72	9.79	—0.07	179.99
12.00 M.	26°.9	26°.2	48.36	44.12	1.01	0.61	0.05	0.02	9.71	9.78	—0.07	179.83
3.00 P.M.	26°.8	26°.3	48.61	44.35	1.01	0.61	0.05	0.02	9.67	9.78	—0.11	180.80

H = 1 Mol. Wt. Glucose = 178.74.

Mean Mol. Wt. 180.21

Table IX.

Original wt. normal concentration of solution, 0.4.
Rotation of original solution, 20°.8.
Rotation at conclusion of experiment, 20°.7.
Percentage loss in concentration, 0.48 per cent.
Calibration units of air in manometer, 442.92.
Time of setting up cell, 4.30 P.M., May 25, 1906.

Experiment No. 2.
Manometer used, No. 13.
Capillary depression, 0.02 atmosphere.
Cell used, D.
Resistance of membrane, 98,000 ohms.
Initial pressure, 9.36 atmospheres.

	Temperature.		Volume of air in manometer.		Corrections.							
Time.	Solution.	Air in manometer.	Uncorrected.	Corrected.	Atmospheric pressure.	Liquids in manometer.	Dilution of cell contents.	Capillary depression.	Osmotic pressure corrected.	Theoretical gas pressure.	Difference between pressure found and calculated.	Mol. Wt. calculated from osmotic pressure.
May 26												
9.00 A.M.	26°.6	26°.5	48.67	44.35	0.99	0.61	0.05	0.02	9.67	9.77	—0.10	180.69
12.00 M.	26°.6	26°.6	48.77	44.43	0.99	0.61	0.05	0.02	9.66	9.77	—0.11	180.88
3.30 P.M.	26°.7	27°.0	48.97	44.55	0.99	0.61	0.05	0.02	9.63	9.78	—0.15	181.49

H = 1 Mol. Wt. Glucose = 178.74. Mean Mol. Wt. 181.02

Table X.

Original wt. normal concentration of solution, 0.5.
Rotation of original solution, 25°.8.
Rotation at conclusion of experiment, 25°.3.
Percentage loss in concentration, 1.94 per cent.
Calibration units of air in manometer, 467.21.
Time of setting up cell, 5.30 P.M., Jan. 22, 1906.

Experiment No. 1.
Manometer used, No. 14.
Capillary depression, 0.02 atmosphere.
Cell used, A.
Resistance of membrane, 184,660 ohms.
Initial pressure.

Time.	Temperature.		Volume of air in manometer.		Corrections.				Osmotic pressure corrected.	Theoretical gas pressure.	Difference between pressure found and calculated.	Mol. Wt. calculated from osmotic pressure.
	Solution.	Air in manometer.	Uncorrected.	Corrected.	Atmospheric pressure.	Liquids in manometer.	Dilution of cell contents.	Capillary depression.				
Jan. 22 9.00 P.M.	21°.20	. . .	78.01									
Jan. 23 9.00 A.M.	21°.40	23°.1	42.81									
12.30 P.M.	21°.45	23°.4	42.31									
3.00 P.M.	21°.60	23°.4	42.15									
5.00 P.M.	21°.62	23°.4	41.96									
8.30 P.M.	21°:70	23°.4	41.78									
Jan. 24 9.10 A.M.	21°.85	22°.2	41.35									
1.00 P.M.	21°.90	22°.7	41.37									
3.00 "	21°.90	22°.6	41.39	38.22	1.01	0.60	0.23	0.02	12.06	12.03	+0.03	178.25
5.00 "	21°.90	22°.8	41.38	38.18	1.01	0.60	0.23	0.02	12.07	12.03	+0.04	178.10
9.00 "	21°.75	22°.4	41.42	38.27	1.01	0.60	0.23	0.02	12.05	12.02	+0.03	178.31
Jan. 25 9.15 A.M.	21°.90	22°.3	41.29	38.16	1.02	0.60	0.23	0.02	12.09	12.03	+0.06	177.81

H = 1 Mol. Wt. Glucose = 178.74. Mean Mol. Wt. 178.12

Table XI.

Original wt. normal concentration of solution, 0.5.
Rotation of original solution, 25°.8.
Rotation at conclusion of experiment, 25°.5.
Percentage loss in concentration, 1.16 per cent.
Calibration units of air in manometer, 441.97.
Time of setting up cell, 12.30 P.M., May 17, 1906.

Experiment No. 2.
Manometer used, No. 8.
Capillary depression, 0.02 atmosphere.
Cell used, D.
Resistance of membrane, 98,000.
Initial pressure, 10 atmospheres.

	Temperature.		Volume of air in manometer.		Corrections.							
Time.	Solution.	Air in manometer.	Uncorrected.	Corrected.	Atmospheric pressure.	Liquids in manometer.	Dilution of cell contents.	Capillary depression.	Osmotic pressure corrected.	Theoretical gas pressure.	Difference between pressure found and calculated.	Mol. Wt. calculated from osmotic pressure.
May 17 11.30 P.M.	23°.8	25°.7	39.78	36.35	1.00	0.66	0.14	0.02	11.98	12.10	—0.12	180.59
May 18 9.00 A.M.	24°.2	25°.6	39.63	36.22	1.00	0.66	0.14	0.02	12.02	12.12	—0.10	180.24
5.00 P.M.	24°.5	26°.6	39.89	36.34	0.99	0.66	0.14	0.02	11.99	12.13	—0.14	180.87

Displacement of manometer = 0.57 mm. Mean Mol. Wt. 180.57

Dilution due to displacement of manometer = 0.08 per cent.

H = 1 Mol. Wt. Glucose = 178.74.

Table XII.

Original wt. normal concentration of solution, 0.6.
Rotation of original solution, 30°.6.
Rotation at conclusion of experiment, 29°.45.
Percentage loss in concentration, 3.76 per cent.
Calibration units of air in manometer, 467.21.
Time of setting up cell, 5.30 P.M., Jan. 25, 1906.

Experiment No. 1.
Manometer used, No. 14.
Capillary depression, 0.02 atmosphere.
Cell used, A.
Resistance of membrane.
Initial pressure, 7.0 atmospheres.

	Temperature.		Volume of air in manometer.		Corrections.							
Time.	Solution.	Air in manometer.	Uncorrected.	Corrected.	Atmospheric pressure.	Liquids in manometer.	Dilution of cell contents.	Capillary depression.	Osmotic pressure corrected.	Theoretical gas pressure.	Difference between pressure found and calculated.	Mol. Wt. calculated from osmotic pressure.
Jan. 25												
9.00 P.M.	21°.96	22°.72	47.71									
Jan. 26												
9.15 A.M.	22°.2	22°.65	37.27									
3.40 P.M.	22°.2	22°.70	36.61									
5.00 "	22°.2	22°.80	36.62									
8.30 "	22°.2	22°.80	36.44									
Jan. 27												
10.30 A.M.	22°.2	22°.80	35.94									
3.00 P.M.	22°.2	22°.82	35.75									
4.45 "	22°.2	23°.00	35.76									
9.00 "	22°.2	22°.90	35.61									
Jan. 28												
12.00 M.	22°.3	22°.80	35.39	32.66	0.99	0.63	0.54	0.02	14.47	14.43	+0.04	178.52
8.00 P.M.	22°.7	22°.80	35.13	32.42	0.99	0.63	0.54	0.02	14.59	14.47	+0.12	177.39
Jan. 29.												
9.00 A.M.	22°.7	22°.75	35.06	32.36	1.00	0.63	0.54	0.02	14.62	14.47	+0.15	176.95

Displacement of manometer = 7.29 mm.
Dilution due to displacement of manometer = 0.94 per cent. Mean Mol. Wt. 177.62
H = 1 Mol. Wt. Glucose = 178.74.

Table XIII.

Original wt. normal concentration of solution, 0.6.
Rotation of original solution, 30°.6.
Rotation at conclusion of experiment, 30°.0.
Percentage loss in concentration, 1.96 per cent.
Calibration units of air in manometer, 467.21.
Time of setting up cell, 5.30 P.M., Feb. 1, 1906.

Experiment No. 2.
Manometer used, No. 14.
Capillary depression, 0.02 atmosphere.
Cell used, A.
Resistance of membrane, 68,250 ohms.
Initial pressure, 6.5 atmospheres.

	Temperature.		Volume of air in manometer.		Corrections.							
Time.	Solution.	Air in manometer.	Uncorrected.	Corrected.	Atmospheric pressure.	Liquids in manometer.	Dilution of cell contents.	Capillary depression.	Osmotic pressure corrected.	Theoretical gas pressure.	Difference between pressure found and calculated.	Mol. Wt. calculated from osmotic pressure.
Feb. 1 8.15 P.M.	22°.40	23°.40	48.23									
Feb. 2 9.00 A.M.	22°.40	23°.36	36.55									
3.00 P.M.	22°.42	23°.36	35.95									
8.30 "	22°.43	22°.58	35.48									
Feb. 3 9.00 A.M.	22°.45	22°.58	35.08	32.42	1.01	0.63	0.28	0.02	14.31	14.40	—0.09	180.60
3.00 P.M.	22°.45	22°.42	35.08	32.41	1.01	0.63	0.28	0.02	14.31	14.40	—0.09	180.60
9.00 P.M.	22°.35	22°.46	35.08	32.41	1.01	0.63	0.28	0.02	14.31	14.39	—0.08	180.54
Feb. 4 10.00 A.M.	22°.35	22°.40	34.95	32.30	1.01	0.63	0.28	0.02	14.36	14.39	—0.03	179.92

H = 1 Mol. Wt. Glucose = 178.74 Mean Mol. Wt. 180.42

Table XIV.

Original wt. normal concentration of solution, 0.6.
Rotation of original solution, 30°.7.
Rotation at conclusion of experiment, 30°.6.
Percentage loss in concentration, 0.32 per cent.
Calibration units of air in manometer, 434.98.
Time of setting up cell, 12.15 P.M., Oct. 13, 1906.

Experiment No. 3.
Manometer used, No. 5.
Capillary depression, 0.02 atmosphere.
Cell used, D.
Resistance of membrane, 108,000 ohms.
Initial pressure, 10.46 atmospheres.

Time.	Temperature.		Volume of air in manometer.		Corrections.							
	Solution.	Air in manometer.	Uncorrected.	Corrected.	Atmospheric pressure.	Liquids in manometer.	Dilution of cell contents.	Capillary depression.	Osmotic pressure corrected.	Theoretical gas pressure.	Difference between pressure found and calculated.	Mol. Wt. calculated from osmotic pressure.
Oct. 13												
3.30 P.M.	22°.3	22°.5	35.30									
10.00 "	22°.3	22°.3	32.17	29.73	1.01	0.64	0.04	0.02	14.32	14.45	—0.13	180.39
Oct. 14												
10.00 A.M.	22°.3	22°.2	32.24	29.81	1.01	0.64	0.04	0.02	14.28	14.45	—0.17	180.89
1.00 P.M.	22°.4	22°.5	32.33	29.86	1.01	0.64	0.04	0.02	14.26	14.46	—0.20	181.21

Displacement of manometer = 0.76 mm.
Dilution due to displacement of manometer = 0.11 per cent.
H = 1 Mol. Wt. Glucose = 178.74 Mean Mol. Wt. 180.83

Table XV.

Original wt. normal concentration of solution, 0.7.
Rotation of original solution, 35°.5.
Rotation at conclusion of experiment, 34°.6.
Percentage loss in concentration, 2.54 per cent.
Calibration units of air in manometer, 467.21.
Time of setting up cell, 5.00 P.M., Feb. 5, 1906.

Experiment No. 1.
Manometer used, No. 14.
Capillary depression, 0.02 atmosphere.
Cell used, A.
Resistance of membrane, 110,600 ohms.
Initial pressure, 5 atmospheres.

Time.	Temperature.		Volume of air in manometer.		Corrections.				Osmotic pressure corrected.	Theoretical gas pressure.	Difference between pressure found and calculated.	Mol. Wt. calculated from osmotic pressure.
	Solution.	Air in manometer.	Uncorrected.	Corrected.	Atmospheric pressure.	Liquids in manometer.	Dilution of cell contents.	Capillary depression.				
Feb. 5 9.00 P.M.	22°.31	22°.71	38.08									
Feb. 6 10.00 A.M.	22°.32	22°.30	30.60									
3.00 P.M.	22°.32	22°.56	30.36									
5.00 "	22°.34	22°.58	30.37									
8.00 "	22°.26	22°.22	30.29									
Feb. 7 9.00 A.M.	22°.32	22°.53	30.20	27.89	1.01	0.62	0.43	0.02	16.81	16.86	—0.05	179.28
12.00 M.	22°.25	22°.66	30.19	27.87	1.01	0.62	0.43	0.02	16.82	16.85	—0.03	179.14
5.00 P.M.	22°.20	22°.46	30.17	27.87	1.01	0.62	0.43	0.02	16.82	16.85	—0.03	179.11

H = 1 Mol. Wt. Glucose = 178.74

Mean Mol. Wt. 179.18

Table XVI.

Original wt. normal concentration of solution, 0.7.
Rotation of original solution, 35°.5.
Rotation at conclusion of experiment, 34°.5.
Percentage loss in concentration, 2.82 per cent.
Calibration units of air in manometer, 473.77.
Time of setting up cell, 4.15 P.M., June 1, 1906.

Experiment No. 2.
Manometer used, No. 11.
Capillary depression, 0.02 atmosphere.
Cell used, G.
Resistance of membrane, 218,000 ohms.
Initial pressure, 14 atmospheres.

Time.	Temperature.		Volume of air in manometer.		Corrections.				Osmotic pressure corrected.	Theoretical gas pressure.	Difference between pressure found and calculated.	Mol. Wt. calculated from osmotic pressure.
	Solution.	Air in manometer.	Uncorrected.	Corrected.	Atmospheric pressure.	Liquids in manometer.	Dilution of cell contents.	Capillary depression.				
June 1 6.20 P.M.	25°.2	25°.9	30.58									
7.30 "	25°.2	25°.9	30.14									
9.00 "	25°.3	25°.8	30.15									
June 2 10.00 A.M.	25°.3	25°.4	30.45	27.85	1.00	0.56	0.47	0.02	17.06	17.03	+0.03	178.45
2.30 P.M.	25°.4	26°.2	30.70	28.01	1.00	0.56	0.47	0.02	16.96	17.04	—0.08	179.56
5.30 P.M.	25°.4	26°.4	30.73	28.02	1.00	0.56	0.47	0.02	16.96	17.04	—0.08	179.56
June 3 10.30 A.M.	25°.6	25°.9	30.85	28.17	1.00	0.56	0.47	0.02	16.87	17.05	—0.18	180.61

Displacement of manometer = 3.24 mm.

Dilution due to displacement of manometer = 0.21 per cent   Mean Mol. Wt. 179.55

H = 1   Mol. Wt. Glucose = 178.74.

Table XVII.

Original wt. normal concentration of solution, 0.7.
Rotation of original solution, 35°.5.
Rotation at conclusion of experiment, 34°.9.
Percentage loss in concentration, 1.69 per cent.
Calibration units of air in manometer, 434.98.
Time of setting up cell, 4.30 P.M., Nov. 12, 1906.

Experiment No. 3.
Manometer used, No. 5.
Capillary depression, 0.02 atmosphere.
Cell used, A.
Resistance of membrane, 110,000 ohms.
Initial pressure, 11.7 atmospheres.

Time.	Temperature.		Volume of air in manometer.		Corrections.				Osmotic pressure corrected.	Theoretical gas pressure.	Difference between pressure found and calculated.	Mol. Wt. calculated from osmotic pressure.
	Solution.	Air in manometer.	Uncorrected.	Corrected.	Atmospheric pressure.	Liquids in manometer.	Dilution of cell contents.	Capillary depression.				
Nov. 12												
9.00 P.M.	22°.7	22°.8	31.41									
Nov. 13												
10.00 A.M.	22°.7	22°.7	29.51									
2.30 P.M.	22°.7	22°.6	28.88									
4.30 "	22°.7	22°.6	28.77									
8.30 "	22°.7	22°.7	28.58									
Nov. 14												
10.00 A.M.	22°.7	22°.5	28.01	25.87	1.00	0.64	0.28	0.02	16.75	16.88	—0.13	180.16
1.00 P.M.	22°.7	22°.7	28.05	25.89	1.00	0.64	0.28	0.02	16.74	16.88	—0.14	180.27
3.30 "	22°.7	22°.9	28.03	25.85	1.00	0.64	0.28	0.02	16.76	16.88	—0.12	180.06

Displacement of manometer = 6.11 mm.

Dilution due to displacement of manometer = 0.84 per cent. Mean Mol. Wt. 180.16

H = 1 Mol. Wt. Glucose = 178.74.

Table XVIII.

Original wt. normal concentration of solution, 0.8.	Experiment No. 1.
Rotation of original solution, 40°.2.	Manometer used, No. 5.
Rotation at conclusion of experiment, 39°.1.	Capillary depression, 0.02 atmosphere.
Percentage loss in concentration, 2.76 per cent.	Cell used, A.
Calibration units of air in manometer, 434.98.	Resistance of membrane, 111,000 ohms.
Time of setting up cell, 4.00 P.M., Nov. 15, 1906.	Initial pressure, 7.2 atmospheres.

Time.	Temperature.		Volume of air in manometer.		Corrections.				Osmotic pressure corrected.	Theoretical gas pressure.	Difference between pressure found and calculated.	Mol. Wt. calculated from osmotic pressure.
	Solution.	Air in manometer.	Uncorrected.	Corrected.	Atmospheric pressure.	Liquids in manometer.	Dilution of cell contents.	Capillary depression.				
Nov. 15												
8.30 P.M.	22°.8	22°.9	41.21									
11.45 "	22°.8	22°.8	27.63									
Nov. 16												
10.00 A.M.	22°.9	22°.7	25.10									
1.00 P.M.	22°.9	22°.9	25.07									
3.30 "	22°.9	22°.9	24.99									
7.30 "	22°.8	22°.9	24.94	23.00	1.00	0.64	0.53	0.02	19.10	19.30	—0.20	
Nov. 17												
10.30 A.M.	23°.0	22°.9	24.73	22.81	1.00	0.64	0.53	0.02	19.26	19.31	—0.05	179.25
2.30 P.M.	23°.0	23°.2	24.74	22.79	1.00	0.64	0.53	0.02	19.28	19.31	—0.03	179.06

Displacement of manometer = 9.82 mm.

Dilution due to displacement of manometer = 1.42 per cent. Mean Mol. Wt. 179.16

H = 1 Mol. Wt. Glucose = 178.74.

Table XIX.

Original wt. normal concentration of solution, 0.8.
Rotation of original solution, $40^\circ.2$.
Rotation at conclusion of experiment, $39^\circ.5$.
Percentage loss in concentration, 1.74 per cent.
Calibration units of air in manometer, 434.93.
Time of setting up cell, 4.15 P.M., Nov. 19, 1906.

Experiment No. 2.
Manometer used, No. 13.
Capillary depression, 0.02 atmosphere.
Cell used, A.
Resistance of membrane, 108,000 ohms.
Initial pressure, 12.8 atmospheres.

	Temperature.		Volume of air in manometer.		Corrections.							
Time.	Solution.	Air in manometer.	Uncorrected.	Corrected.	Atmospheric pressure.	Liquids in manometer.	Dilution of cell contents.	Capillary depression.	Osmotic pressure corrected.	Theoretical gas pressure.	Difference between pressure found and calculated.	Mol. Wt. calculated from osmotic pressure.
Nov. 19												
9.45 P.M.	$22^\circ.9$	$23^\circ.9$	26.56									
Nov. 20												
10.30 A.M.	$23^\circ.0$	$23^\circ.1$	25.26									
1.00 P.M.	$23^\circ.0$	$23^\circ.5$	25.21									
4.15 "	$23^\circ.1$	$23^\circ.8$	25.10									
Nov. 21												
10.00 A.M.	$23^\circ.1$	$22^\circ.7$	24.79									
2.15 P.M.	$23^\circ.1$	$23^\circ.3$	24.77	22.82	1.00	0.64	0.34	0.02	19.06	19.32	—0.26	
4.30 "	$23^\circ.1$	$23^\circ.7$	24.72	22.74	1.00	0.64	0.34	0.02	19.13	19.32	—0.19	180.53
Nov. 22												
10.00 A.M.	$23^\circ.4$	$23^\circ.6$	24.67	22.70	1.00	0.64	0.34	0.02	19.16	19.34	—0.18	180.43
12.00 M.	$23^\circ.5$	$23^\circ.9$	24.65	22.66	1.00	0.64	0.34	0.02	19.19	19.35	—0.16	180.21

Displacement of manometer = 2.11 mm.

Dilution due to displacement of manometer = 0.30 per cent. Mean Mol. Wt. 180.39

H = 1 Mol. Wt. Glucose = 178.74.

Table XX.

Original wt. normal concentration of solution, 0.8.
Rotation of original solution, $40^\circ.2$.
Rotation at conclusion of experiment, $39^\circ.5$.
Percentage loss in concentration, 1.74 per cent.
Calibration units of air in manometer, 396.89.
Time of setting up cell, 4.30 P.M., Nov. 23, 1906.

Experiment No. 3.
Manometer used, No. 6.
Capillary depression, 0.02 atmosphere.
Cell used, A.
Resistance of membrane, 155,000.
Initial pressure, 12.1 atmospheres.

Time.	Temperature.		Volume of air in manometer.		Corrections.				Osmotic pressure corrected.	Theoretical gas pressure.	Difference between pressure found and calculated.	Mol. Wt. calculated from osmotic pressure.
	Solution.	Air in manometer.	Uncorrected.	Corrected.	Atmospheric pressure.	Liquids in manometer.	Dilution of cell contents.	Capillary depression.				
Nov. 23												
7.30 P.M.	$23^\circ.6$	$23^\circ.6$	24.73									
Nov. 24												
4.20 A.M.	$23^\circ.6$	$23^\circ.3$	22.81									
11.00 "	$23^\circ.6$	$23^\circ.1$	22.61									
3.00 P.M.	$23^\circ.6$	$23^\circ.6$	22.71									
Nov. 25												
10.30 A.M.	$23^\circ.7$	$23^\circ.1$	22.44	20.68	1.00	0.67	0.34	0.02	19.22	19.36	—0.14	180.05
3.00 P.M.	$23^\circ.6$	$23^\circ.4$	22.45	20.67	1.00	0.67	0.34	0.02	19.23	19.35	—0.12	179.89
9.30 P.M.	$23^\circ.7$	$23^\circ.4$	22.42	20.64	1.00	0.67	0.34	0.02	19.26	19.36	—0.10	179.67
Nov. 26												
10.45 A.M.	$23^\circ.6$	$23^\circ.1$	22.38	20.63	1.00	0.67	0.34	0.02	19.27	19.35	—0.08	179.52
2.30 P.M.	$23^\circ.6$	$23^\circ.7$	22.42	20.63	1.00	0.67	0.34	0.02	19.27	19.35	—0.08	179.52

Displacement of manometer = 2.12 mm.

Dilution due to displacement of manometer = 0.30 per cent. Mean Mol. Wt. 179.73

H = 1 Mol. Wt. Glucose = 178.74.

Table XXI.

Original wt. normal concentration of solution, 0.9.
Rotation of original solution, 44°.85.
Rotation at conclusion of experiment, 44°.20.
Percentage loss in concentration, 1.45 per cent.
Calibration units of air in manometer, 434.93.
Time of setting up cell, 4.00 P.M., Nov. 27, 1906.

Experiment No. 1.
Manometer used, No. 13.
Capillary depression, 0.02 atmosphere.
Cell used, A.
Resistance of membrane, 138,000 ohms.
Initial pressure, 16.5 atmospheres.

	Temperature.		Volume of air in manometer.		Corrections.							
Time.	Solution.	Air in manometer.	Uncorrected.	Corrected.	Atmospheric pressure.	Liquids in manometer.	Dilution of cell contents.	Capillary depression-	Osmotic pressure corrected.	Theoretical gas pressure.	Difference between pressure found and calculated.	Mol. Wt. calculated from osmotic pressure.
Nov. 27 10.30 P.M.	23°.8	24°.1	22.29									
Nov. 28 10.30 A.M.	23°.9	24°.1	22.08									
2.15 P.M.	23°.9	24°.1	22.11									
5.00 "	24°.0	24°.3	22.07									
8.30 "	24°.0	24°.1	22.01									
Nov. 29 10.00 A.M.	24°.1	23°.9	21.98									
2.00 P.M.	24°.1	23°.6	21.99									
7.00 "	24°.1	23°.6	21.91	20.16	1.01	0.65	0.31	0.02	21.55	21.81	—0.26	..
Nov. 30 11.00 A.M.	23°.7	22°.8	21.77	20.09	1.00	0.65	0.31	0.02	21.64	21.79	—0.15	179.90
5.00 P.M.	23°.7	23°.7	21.83	20.08	1.00	0.65	0.31	0.02	21.64	21.79	—0.15	179.90
Dec. 1 9.30 A.M.	23°.7	23°.5	21.80	20.07	1.00	0.65	0.31	0.02	21.65	21.79	—0.14	179.82

Displacement of manometer = 2.57 mm.

Dilution due to displacement of manometer = 0.35 per cent.

Mean Mol. Wt. 179.87

H = 1 Mol. Wt. Glucose = 178.74.

Table XXII.

Original wt. normal concentration of solution, 0.9.
Rotation of original solution, 44°.85.
Rotation at conclusion of experiment, 44°.4.
Percentage loss in concentration, 1.00 per cent.
Calibration units of air in manometer, 396.89.
Time of setting up cell, 4.00 P.M., Dec. 3, 1906.

Experiment No. 2.
Manometer used, No. 6.
Capillary depression, 0.02 atmosphere.
Cell used, A.
Resistance of membrane, 183,000.
Initial pressure, 14.7 atmospheres.

Time.	Temperature.		Volume of air in manometer.		Corrections.				Osmotic pressure corrected.	Theoretical gas pressure.	Difference between pressure found and calculated.	Mol. Wt. calculated from osmotic pressure.
	Solution.	Air in manometer.	Uncorrected.	Corrected.	Atmospheric pressure.	Liquids in manometer.	Dilution of cell contents.	Capillary depression.				
Dec. 3 8.00 P.M.	22°.3	22°.7	21.28									
Dec. 4 10.00 A.M.	22°.4	22°.3	19.96									
2.00 P.M.	22°.5	22°.8	19.95	18.41	1.00	0.67	0.22	0.02	21.47	21.69	—0.22	180.59
5.00 "	22°.5	22°.7	19.95	18.41	1.00	0.67	0.22	0.02	21.47	21.69	—0.22	180.59
10.00 "	22°.5	23°.2	19.98	18.41	1.00	0.67	0.22	0.02	21.47	21.69	—0.22	180.59
Dec. 5 9.00 A.M.	22°.7	22°.7	19.91	18.38	1.00	0.67	0.22	0.02	21.50	21.71	—0.21	180.47
2.00 P.M.	22°.7	23°.4	19.94	18.36	1.00	0.67	0.22	0.02	21.53	21.71	—0.18	180.21

Displacement of manometer = 0.98 mm.

Dilution due to displacement of manometer = 0.12 per cent. Mean Mol. Wt. 180.49

H = 1 Mol. Wt. Glucose = 178.74.

Table XXIII.

Original wt. normal concentration of solution, 0.9.	Experiment No. 3.
Rotation of original solution, 44°.85.	Manometer used, No. 13.
Rotation at conclusion of experiment, 44°.55.	Capillary depression, 0.02 atmosphere.
Percentage loss in concentration, 0.66 per cent.	Cell used, A.
Calibration units of air in manometer, 434.93.	Resistance of membrane, 160,000 ohms.
Time of setting up cell, 3.45 P.M., Dec. 6, 1906.	Inital pressure, 15.8 atmospheres.

Time.	Temperature.		Volume of air in manometer.		Corrections.				Osmotic pressure corrected.	Theoretical gas pressure.	Difference between pressure found and calculated.	Mol. Wt. calculated from osmotic pressure.
	Solution.	Air in manometer.	Uncorrected.	Corrected.	Atmospheric pressure.	Liquids in manometer.	Dilution of cell contents.	Capillary depression.				
Dec. 6 8.30 P.M.	22°.8	23°.9	22.46									
Dec. 7 10.00 A.M.	23°.0	23°.3	21.65	19.94	1.00	0.65	0.14	0.02	21.63	21.73	—0.10	179.56
2.30 P.M.	23°.1	23°.3	21.69	19.98	1.00	0.65	0.14	0.02	21.58	21.74	—0.16	180.04
4.30 "	23°.1	23°.2	21.64	19.94	1.00	0.65	0.14	0.02	21.63	21.74	—0.11	179.62
Dec. 8 12.00 M.	23°.1	22°.8	21.58	19.91	1.01	0.65	0.14	0.02	21.65	21.74	—0.09	179.46
3.00 P.M.	23°.1	23°.3	21.59	19.89	1.01	0.65	0.14	0.02	21.67	21.74	—0.07	179.30

Displacement of manometer = 1.69 mm.

Dilution due to displacement of manometer = 0.23 per cent. Mean Mol. Wt. 179.60

H = 1 Mol. Wt. Glucose 178.74.

Table XXIV.

Original wt. normal concentration of solution, 1.0.
Rotation of original solution, 49°.4.
Rotation at conclusion of experiment, 48°.95.
Percentage loss in concentration, 0.91 per cent.
Calibration units of air in manometer, 434.93.
Time of setting up cell, 11.30 A.M., Dec. 12, 1906.

Experiment No. 1.
Manometer used, No. 13.
Capillary depression, 0.02 atmosphere.
Cell used, A.
Resistance of membrane, 220,000 ohms.
Initial pressure, 15 atmospheres.

Time.	Temperature.		Volume of air in manometer.		Corrections.				Osmotic pressure corrected.	Theoretical gas pressure.	Difference between pressure found and calculated.	Mol. Wt. calculated from osmotic pressure.
	Solution.	Air in manometer.	Uncorrected.	Corrected.	Atmospheric pressure.	Liquids in manometer.	Dilution of cell contents.	Capillary depression.				
Dec. 12												
8.45 P.M.	22°.0	22°.2	19.53									
Dec. 13												
10.00 A.M.	22°.0	21°.8	19.46									
4.45 P.M.	22°.0	22°.7	19.46	17.96	1.00	0.65	0.22	0.02	24.11	24.06	+0.05	178.38
11.00 "	22°.1	22°.2	19.44	17.97	1.00	0.65	0.22	0.02	24.09	24.07	+0.02	178.59
Dec. 14												
10.45 A.M.	22°.3	23°.0	19.44	17.92	1.01	0.65	0.22	0.02	24.16	24.09	+0.07	178.20
2.15 P.M.	22°.3	22°.6	19.45	17.96	1.01	0.65	0.22	0.02	24.11	24.09	+0.02	178.57
5.00 "	22°.3	22°.5	19.44	17.96	1.01	0.65	0.22	0.02	24.11	24.09	+0.02	178.57

Displacement of manometer = 1.49 mm.

Dilution due to displacement of manometer = 0.20 per cent. Mean Mol. Wt. 178.46

H = 1 Mol. Wt. Glucose = 178.74.

Table XXV.

Original wt. normal concentration of solution, 1.0.
Rotation of original solution, 49°.4.
Rotation at conclusion of experiment, 48°.95.
Percentage loss in concentration, 0.91 per cent.
Calibration units of air in manometer, 396.89.
Time of setting up cell, 12.00 M., Dec. 9, 1906.

Experiment No. 2.
Manometer used, No. 6.
Capillary depression, 0.02 atmosphere.
Cell used, A.
Resistance of membrane, 270,000 ohms.
Initial pressure, 14.5 atmospheres.

Time.	Temperature.		Volume of air in manometer.		Corrections.				Osmotic pressure corrected.	Theoretical gas pressure.	Difference between pressure found and calculated.	Mol. Wt. calculated from osmotic pressure.
	Solution.	Air in manometer.	Uncorrected.	Corrected.	Atmospheric pressure.	Liquids in manometer.	Dilution of cell contents.	Capillary depression.				
Dec. 9												
4.30 P.M.	22°.6	22°.3	18.28									
11.30 "	22°.6	22°.1	17.86									
Dec. 10												
10.00 A.M.	22°.6	23°.5	17.90	16.48	1.01	0.67	0.22	0.02	23.98	24.11	—0.13	179.71
2.30 P.M.	22°.6	23°.3	17.88	16.47	1.00	0.67	0.22	0.02	24.00	24.11	—0.11	179.57
5.30 "	22°.6	23°.3	17.87	16.46	1.00	0.67	0.22	0.02	24.02	24.11	—0.09	179.42
Dec. 11												
10.30 A.M.	22°.7	23°.2	17.88	16.47	1.01	0.67	0.22	0.02	23.99	24.12	—0.13	179.70

Displacement of manometer = 1.56 mm.

Dilution due to displacement of manometer = 0.14 per cent. Mean Mol. Wt. 179.60

H = 1 Mol. Wt. Glucose = 178.74.

Table XXVI.

Original wt. normal concentration of solution, 1.0.
Rotation of original solution, 49°.4.
Rotation at conclusion of experiment, 48°.55.
Percentage loss in concentration, 1.72 per cent.
Calibration units of air in manometer, 396.89.
Time of setting up cell, 12.30 P.M., Dec. 15, 1906.

Experiment No. 3.
Manometer used, No. 6.
Capillary depression, 0.02 atmosphere.
Cell used, A.
Resistance of membrane, 185,000 ohms.
Initial pressure, 13.9 atmospheres.

Time.	Temperature.		Volume of air in manometer.		Corrections.				Osmotic pressure corrected.	Theoretical gas pressure.	Difference between pressure found and calculated.	Mol. Wt. calculated from osmotic pressure.
	Solution.	Air in manometer.	Uncorrected.	Corrected.	Atmospheric pressure.	Liquids in manometer.	Dilution of cell contents.	Capillary depression.				
Dec. 15 6.00 P.M.	22°.1	22°.2	18.28									
8.15 “	22°.1	22°.1	18.07									
Dec. 16 9.00 A.M.	22°.1	21°.9	18.00									
1.30 P.M.	22°.1	21°.8	18.03									
10.00 “	22°.1	22°.0	17.96	16.62	1.00	0.67	0.41	0.02	23.98	24.07	—0.09	179.41
Dec. 17 10.15 A.M.	22°.1	22°.1	17.91	16.56	1.00	0.67	0.41	0.02	24.06	24.07	—0.01	178.81
12.30 P.M.	22°.1	22°.1	17.93	16.58	1.00	0.67	0.41	0.02	24.04	24.07	—0.03	178.96
5.00 “	22°.1	22°.2	17.94	16.59	1.00	0.67	0.41	0.02	24.02	24.07	—0.05	179.11

Displacement of manometer = 1.24 mm.

Dilution due to displacement of manometer = 0.17 per cent. Mean Mol. Wt. 179.07

H = 1 Mol. Wt. Glucose = 178.74.

Series I., 1900.

Weight normal concentration.	No. of experiment.	Temperature of solution.			Osmotic pressure observed (atmospheres).			Calculated gas pressure for same temperature.			Difference between mean osmotic and mean gas pressure.	Molecular weight calculated from osmotic pressure.			Mean molecular weight for each concentration.
		Mean.	Highest.	Lowest.	Mean.	Highest.	Lowest.	Mean.	Highest.	Lowest.		Mean.	Highest.	Lowest.	
0.1	1	24°.10	24°.40	23°.90	2.39	2.39	2.38	2.42	2.43	2.42	—0.03	181.40	182.00	181.10	
"	2	25°.10	25°.20	25°.00	2.42	2.42	2.41	2.43	2.43	2.43	—0.01	179.83	180.30	179.50	180.62
0.2	1	24°.10	24°.20	24°.00	4.76	4.79	4.75	4.85	4.85	4.85	—0.09	181.77	182.30	180.70	
"	2	24°.93	25°.20	24°.70	4.77	4.78	4.76	4.86	4.86	4.86	—0.09	182.10	182.60	181.60	181.94
0.3	1	22°.20	22°.30	22°.20	7.12	7.15	7.08	7.22	7.22	7.22	—0.10	181.38	182.30	180.50	
"	2	23°.48	23°.60	23°.30	7.17	7.19	7.16	7.25	7.26	7.25	—0.08	180.73	181.10	180.30	181.06
0.4	1	26°.90	27°.00	26°.80	9.70	9.72	9.67	9.78	9.79	9.78	—0.08	180.21	180.80	179.83	
"	2	26°.60	26°.70	26°.60	9.65	9.67	9.63	9.77	9.78	9.77	—0.12	181.02	181.49	180.69	180.62
0.5	1	21°.86	21°.90	21°.75	12.07	12.09	12.05	12.03	12.03	12.02	+0.04	178.12	178.31	177.81	
"	2	24°.17	24°.50	23°.80	12.00	12.02	11.98	12.12	12.13	12.10	—0.12	180.57	180.87	180.24	179.35
0.6	1	22°.57	22°.70	23°.30	14.56	14.62	14.47	14.46	14.47	14.43	+0.10	177.62	178.52	176.95	
"	2	22° 40	22°.45	22°.35	14.32	14.36	14.31	14.40	14.40	14.39	—0.08	180.42	180.60	179 92	
"	3	22°.30	22°.40	22°.30	14.29	14.32	14.26	14.45	14.46	14.45	—0.16	180.83	181.21	180.39	179.62
0.7	1	22°.26	22°.32	22°.20	16.82	16.82	16.81	16.85	16.86	16.85	—0.03	179.18	179.28	179.11	
"	2	25°.43	25°.60	25°.30	16.96	17.06	16.87	17.04	17.05	17.03	—0.08	179.55	180.61	178.45	
"	3	22°.70	22°.70	22°.70	16.75	16.76	16.74	16.88	16.88	16.88	—0.13	180.16	180.27	180.06	179.63
0.8	1	23°.00	23°.00	23°.00	19.27	19.28	19.26	19.31	19.31	19.31	—0.04	179.16	179.25	179.06	
"	2	23°.28	23°.50	23°.10	19.16	19.19	19.13	19.33	19.35	19.32	—0.17	180.39	180.53	180.21	
"	3	23°.64	23°.70	23°.60	19.25	19.27	19.22	19.35	19.36	19.35	—0.10	179.73	180.05	179.52	179.76
0.9	1	23°.80	24°.10	23°.70	21.64	21.65	21.64	21.80	21.81	21.79	—0.16	179.87	179.90	179.82	
"	2	22°.58	22°.70	22°.50	21.49	21.53	21.47	21.70	21.71	21.69	—0.21	180.49	180.59	180.21	
"	3	23°.10	23°.10	23°.00	21.63	21.67	21.58	21.74	21.74	21.73	—0.11	179.60	180.04	179.30	179.99
1.0	1	22°.20	22°.30	22°.00	24.12	24.16	24.09	24.08	24.09	24.06	+0.04	178.46	178.59	178.20	
"	2	22°.60	22°.70	22°.60	24.00	24.02	23.98	24.11	24.12	24.11	—0.11	179.60	179.71	179.42	
"	3	22°.10	22°.10	22°.10	24.03	24.06	23.98	24.07	24.07	24.07	—0.04	179.07	179.41	178.81	179.04

H = 1 Mol. Wt. Glucose = 178.74 Mean Mol. Wt. 180.08

Table XXVIII.—Determination of the Osmotic Pressure of Glucose.

Series I., 1906. Summary of Results.

Weight normal concentration.	No. of experiment.	Temperature of solution.	Observed osmotic pressure. Atmospheres.	Theoretical gas pressure at same temperature. Atmospheres.	Difference between osmotic and gas pressure.	Molecular weight calculated from osmotic pressure.	Mean molecular weight for each concentration.
0.1	1	24°.10	2.39	2.42	—0.03	181.40	
"	2	25°.10	2.42	2.43	—0.01	179.83	180.62
0.2	1	24°.10	4.76	4.85	—0.09	181.77	
"	2	24°.93	4.77	4.86	—0.09	182.10	181.94
0.3	1	22°.20	7.12	7.22	—0.10	181.38	
"	2	23°.48	7.17	7.25	—0.08	180.73	181.06
0.4	1	26°.90	9.70	9.78	—0.08	180.21	
"	2	26°.60	9.65	9.77	—0.12	181.02	180.62
0.5	1	21°.86	12.07	12.03	+0.04	178.12	
"	2	24°.17	12.00	12.12	—0.12	180.57	179.35
0.6	1	22°.57	14.56	14.46	+0.10	177.62	
"	2	22°.40	14.32	14.40	—0.08	180.42	
"	3	22°.30	14.29	14.45	—0.16	180.83	179.62
0.7	1	22°.26	16.82	16.85	—0.03	179.18	
"	2	25°.43	16.96	17.04	—0.08	179.55	
"	3	22°.70	16.75	16.88	—0.13	180.16	179.63
0.8	1	23°.00	19.27	19.31	—0.04	179.16	
"	2	23°.28	19.16	19.33	—0.17	180.39	
"	3	23°.64	19.25	19.35	—0.10	179.73	179.76
0.9	1	23°.80	21.64	21.80	—0.16	179.87	
"	2	22°.58	21.49	21.70	—0.21	180.49	
"	3	23°.10	21.63	21.74	—0.11	179.60	179.99
1.0	1	22°.20	24.12	24.08	+0.04	178.46	
"	2	22°.60	24.00	24.11	—0.11	179.60	
"	3	22°.10	24.03	24.07	—0.04	179.07	179.04

H = 1 Mol. Wt. Glucose = 178.74 Mean Mol. Wt. 180.08

give for cane sugar[1] the information which is embodied for glucose in Table XXVIII.

Finally, in Table XXXI., all the results which have been obtained up to the present time, at temperatures between 18° and 26°, both for cane sugar and for glucose, are brought together in the from of ratios of osmotic to calculated gas pressure at the same temperatures.

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[1] This Journal, 34, 1; 36, 39.

Table XXIX.—Determination of the Osmotic Pressure of Cane Sugar.

Series I., 1905. Summary of Results.

Weight normal concentration.	No. of experiment.	Temperature of solution.	Observed osmotic pressure. Atmospheres.	Theoretical gas pressure at same temperature. Atmospheres.	Differences between osmotic and gas pressure.	Molecular weight calculated from osmotic pressure.	Mean molecular weight for each concentration
0.1	1	18°.85	2.43	2.38	+0.05	334.47	
"	2	18°.71	2.42	2.38	+0.05	334.08	334.28
0.2	1	20°.59	4.73	4.79	—0.06	344.50	
"	2	20°.91	4.79	4.80	—0.01	340.03	342.27
0.25	1	23°.45	6.08	6.05	+0.03	338.05	
"	2	21°.46	5.94	6.02	—0.08	344.60	341.33
0.3	1	19°.28	7.18	7.17	+0.01	339.44	
"	2	17°.65	7.18	7.13	+0.05	337.65	338.55
0.4	1	18°.88	9.45	9.55	—0.10	343.21	
"	2	20°.94	9.65	9.61	+0.04	338.54	340.88
0.5	1	20°.84	11.93	12.01	—0.08	341.92	
"	2	20°.32	12.06	11.99	+0.07	337.85	339.89
0.6	1	21°.38	14.22	14.45	—0.23	345.09	
"	2	24°.45	14.37	14.59	—0.22	344.89	344.99
0.7	1	20°.14	16.66	16.77	—0.11	342.18	
"	2	24°.62	16.89	17.03	—0.14	342.41	342.30
0.8	1	17°.89	19.20	19.03	+0.17	336.46	
"	2	19°.56	19.35	19.13	+0.22	335.86	336.16
0.89101	1	19°.34	21.03	21.30	—0.27	343.90	343.90
0.9	1	19°.84	21.68	21.55	+0.13	337.55	337.55
1.0	1	23°.32	24.56	24.26	+0.30	335.50	
"	2	22°.44	24.28	24.15	+0.13	337.95	
"	3	21°.60	24.17	24.09	+0.08	338.54	337.33
H = 1.				Final mean of Mol. Wts.,			339.95
				Theoretical Mol. Wt.,			339.60

It is clear, as it was in the case of cane sugar,[1] that *glucose in aqueous solution, at temperatures in the vicinity of 20°, exerts an osmotic pressure equal to that which a molecular-equivalent quantity of a gas would exert if its volume were reduced, at the same temperature, to that of the solvent in the pure state.* This rule holds equally well throughout all the concentrations whose pressure we have measured, and the deviations from it do not exceed the known but unavoidable experimental errors of the work.

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[1] This Journal, 34, 93; 36, 87.

Table XXX.—Determination of the Osmotic Pressure of Cane Sugar.

Series II., 1906. Summary of Results.

Weight normal concentration.	No. of experiment.	Temperature of solution.	Observed osmotic pressure. Atmospheres.	Theoretical gas pressure at same temperature. Atmospheres.	Difference between osmotic and gas pressure.	Molecular weight calculated from osmotic pressure.	Mean molecular weight for each concentration.
0.1	1	24°.06	2.51	2.42	+0.09	327.85	
"	2	24°.23	2.55	2.43	+0.12	322.56	325.21
0.2	1	20°.90	4.72	4.79	—0.07	344.96	
"	2	21°.38	4.78	4.80	—0.02	344.90	
"	3	21°.77	4.81	4.81	0.00	339.74	341.87
0.3	1	21°.67	7.24	7.21	+0.03	338.37	
"	2	19°.88	7.20	7.16	+0.04	338.20	338.29
0.4	1	21°.63	9.64	9.61	+0.03	338.73	
"	2	22°.15	9.69	9.63	+0.06	337.50	338.12
0.5	1	22°.62	12.06	12.06	0.00	339.59	
"	2	23°.70	12.23	12.10	+0.13	336.19	337.89
0.6	1	24°.38	14.74	14.55	+0.19	335.32	
"	2	24°.24	14.70	14.55	+0.15	336.07	
"	3	24°.10	14.77	14.54	+0.23	334.32	335.24
0.7	1	23°.64	16.95	16.94	+0.01	339.39	
"	2	23°.90	16.96	16.93	+0.03	339.50	339.45
0.8	1	23°.60	19.30	19.35	—0.05	340.48	
"	2	23°.69	19.39	19.36	+0.03	339.08	339.78
0.9	1	24°.79	21.82	21.86	—0.04	340.19	
"	2	24°.76	21.91	21.86	+0.05	338.82	339.51
1.0	1	23°.56	24.42	24.19	+0.23	336.39	
"	2	24°.58	23.98	24.28	—0.30	342.72	339.56

H = 1 Final mean of Mol. Wts., 337.49

Theoretical Mol. Wt., 339.60

In papers soon to follow this, it will be shown that at temperatures near the freezing point of the solvent, neither cane sugar nor glucose obeys the rule formulated above, that both substances, in the neighborhood of 0°, exert pressures somewhat in excess of the calculated gas pressures.

A second and important conclusion which is to be drawn from the results is that, at the temperatures at which the measurements were made (*i. e.*, between 18° and 26°, in round numbers), both cane sugar and glucose in solution are in the

Table XXXI.—Ratio of Observed Osmotic to Calculated Gas Pressure at the Same Temperature, the Volume of the Gas Being That of the Solvent in the Pure State.

Weight normal concentration.	No. of experiment.	Cane Sugar. Series I.		Cane Sugar. Series II.		Glucose. Series I.	
		Temperature.	Ratio.	Temperature.	Ratio.	Temperature.	Ratio.
0.1	1	18°.85	1.021	24°.06	1.037	24°.10	0.988
"	2	18°.71	1.017	24°.23	1.049	25°.10	0.996
0.2	1	20°.59	0.987	20°.90	0.985	24°.10	0.981
"	2	20°.91	0.998	21°.38	0.996	24°.93	0.981
"	3			21°.77	1.000		
0.25	1	23°.45	1.005				
"	2	21°.46	0.987				
0.3	1	19°.28	1.001	21°.67	1.004	22°.20	0.986
"	2	17°.65	1.007	19°.88	1.006	23°.48	0.989
0.4	1	18°.81	0.990	21°.63	1.003	26°.90	0.992
"	2	20°.94	1.004	22°.15	1.006	26°.60	0.988
0.5	1	20°.84	0.993	22°.62	1.000	21°.86	1.003
"	2	20°.32	1.006	23°.70	1.010	24°.17	0.990
0.6	1	21°.38	0.984	24°.38	1.013	22°.57	1.007
"	2	24°.45	0.984	24°.70	1.010	22°.46	0.994
"	3			24°.10	1.016	22°.30	0.988
0.7	1	20°.14	0.993	23°.64	1.000	22°.26	0.998
"	2	24°.62	0.992	23°.90	1.002	25°.43	0.995
"	3					22°.70	0.992
0.8	1	17°.89	1.009	23°.60	0.997	23°.00	0.998
"	2	19°.56	1.012	23°.69	1.002	23°.28	0.991
"	3					23°.64	0.995
0.89101	1	19°.34	0.987				
0.9	1	19°.84	1.006	24°.79	0.998	23°.80	0.993
"	2			24°.76	1.002	22°.58	0.990
"	3					23°.10	0.995
1.0	1	23°.32	1.012	23°.56	1.010	22°.20	1.002
"	2	22°.44	1.005	24°.58	0.988	22°.60	0.995
"	3	21°.60	1.003			22°.10	0.998

anhydrous condition; for it requires only a very elementary course of reasoning to show that, if solutions made up, as ours are, with a fixed mass of the solvent, exhibit an osmotic pressure strictly proportional to their supposed concentration, the dissolved material cannot have appropriated any portion of the solvent. The only alternative, apparently, is the proposition that the absolute amount of water abstracted from the solvent is the same for all solutions, *i. e.*, wholly independent of concentration.

The Depression of the Freezing Points of Glucose Solutions.

The following table (XXXII.) gives for each weight-normal concentration of our glucose solutions (1) the observed depression of the freezing point, (2) the molecular lowering of the freezing point, (3) the density at 0°. The thermometer which was used in this part of the work has been described in connection with similar data for cane sugar.[1] It had been tested at the "*Reichsanstalt*," and further corrections were made for the subsequent shrinkage of the bulb.

Table XXXII.

Weight normal concentration.	Observed depression of the freezing point.	Molecular lowering of the freezing point.	Density of the solution at 0°.
0.1	0°.192	1.92	1.00687
0.2	0°.386	1.92	1.01376
0.3	0°.576	1.92	1.02041
0.4	0°.762	1.91	1.02691
0.5	0°.952	1.91	1.03327
0.6	1°.147	1.91	1.03945
0.7	1°.337	1.91	1.04551
0.8	1°.528	1.91	1.05143
0.9	1°.720	1.91	1.05731
1.0	1°.918	1.92	1.06300

The notable feature of the data presented in the table is the proportionality of the freezing point depressions to the weights of glucose dissolved in the fixed quantity of water, which relation, like the similar one between osmotic pressure and concentration, at higher temperatures, may be interpreted as indicating that glucose does not, even at the freezing temperatures of its aqueous solutions, appropriate any portion of the solvent. The bearing of this relation upon the question of hydration in solution will be brought forward again in connection with the osmotic pressures which glucose and cane sugar solutions have been found to exert in the vicinity of 0°.

JOHNS HOPKINS UNIVERSITY,
December 24, 1906.

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[1] THIS JOURNAL, 36, 89.

ON SOME SEMICARBAZIDE DERIVATIVES OF ISOPROPIONIC ACID, BENZOIC ACID AND BENZENESULPHONIC ACID.

By S. F. Acree.

(NINTH COMMUNICATION ON THE URAZOLES.)

[The writer is indebted to the Carnegie Institution, of Washington, for aid in this work.]

In order to pursue some of the physical chemical problems connected with the semicarbazides and urazoles,[1] now being studied in this laboratory, it became necessary to attempt to prepare a number of these substances having greater solubilities in water and in alcohol than do most phenylsemicarbazide and phenylurazole derivatives.

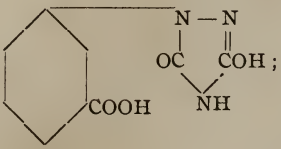
Especially is it desirable to investigate a large number of semicarbazide derivatives of fatty and aromatic acids, such as the following:

I. $NH_2CONHNHCH(CH_3)COOH$;

II. $NH_2CONHNHC_6H_4COOH$;

III. $NH_2CONHNHC_6H_4SO_3H$;

and also a number of corresponding triazole and urazole derivatives, such as



IV.

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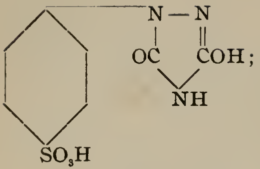
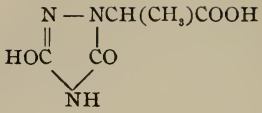
[1] This Journal, **27**, 118; **31**, 185; **32**, 606; **37**, 71. Ber. d. chem. Ges., **35**, 553; **36**, 3139; **37**, 184, 618.

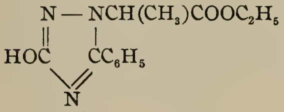


V.

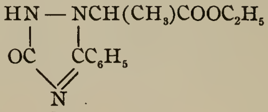


VI.

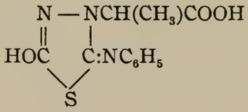
The writer, in conjunction with J. R. Bailey,[1] prepared a number of 1-*iso*propionic acid 3-oxy-5-alkyltriazoles, and their corresponding esters and salts, and also some derivatives of 1,5-dihydro-3-oxy-5-phenylimido-4,1,2-thiodiazole-1-propionic acid (IX.). The ethyl 3-oxy-5-phenyl-1-isopropionate occurs in two modifications, one of which seems to be an enol form, VII., and the other a keto form, VIII.



VII.



VIII.



IX.

All these substances, with an acid side chain, have proved to be more soluble in water than phenylurazole, and physical chemical investigations are being made on them and their derivatives. The influence of the acids in the side group on the amide groups of the urazole and triazole rings, and the simultaneous change in tautomeric relationships, will be made special subjects of investigation. The corresponding thiosemicarbazides, thiourazoles and thiotriazoles will be made and studied in this connection, and various phenylurazoles with basic groups attached to the benzene ring will be investigated from the same standpoints.

[1] Ber. d. chem. Ges., 33, 1520; J. Am. Chem. Soc., 26, 1016.

p-Hydrazinobenzenesulphonic Acid, $H_2NNHC_6H_4SO_3H$.—This substance was prepared according to the following modification of Richter's method:[1] Thirty grams of phenylhydrazine were added to 180 grams of concentrated sulphuric acid; the white precipitate of the salt redissolved when the mixture was stirred and heated. The solution was heated 15 minutes at 100°, and it then began to foam. The mixture was poured into 200 cc. of water and stirred well and cooled, whereupon a pinkish precipitate of *p*-hydrazinebenzenesulphonic acid was formed. This was filtered and dissolved in the necessary amount of 10 per cent sodium hydroxide solution, filtered, and an excess of sodium hydroxide was added. A heavy precipitate of the sodium salt was formed, which is not very soluble in cold water, but readily soluble in hot water. When a solution of this sodium salt was made acid the *p*-hydrazinebenzenesulphonic acid precipitated out pure.

The sodium salt is white. A solution of silver nitrate, when added to one of the sodium salt, is reduced instantly. Analysis:

1.1950 gram sodium salt lost 0.1685 gram H_2O when heated three hours at 140°.

0.1930 gram crystallized salt required 6.84 cc. of 1.125 0.1 N HCl (methyl orange).

	Calculated for $C_6H_7N_2SO_3Na.2H_2O$.	Found.
H_2O	14.62	14.10
Na	9.36	9.19

α-Semicarbazido-p-Benzenesulphonic Acid, $NH_2CONHNHC_6H_4SO_3H$.—When 5 grams of *p*-hydrazinobenzenesulphonic acid were warmed with a solution of one molecular proportion of potassium cyanate in a small amount of water, all of the acid dissolved. When the solution was cooled, crystals of the potassium salt began to appear and when alcohol was added 5.75 grams of pure white potassium semicarbazido-*p*-benzenesulphonate precipitated out. When a concentrated solution of some of this salt was treated with an excess of concentrated hydrochloric acid, a precipitate of the semicarbazido-*p*-benzenesulphonic acid was formed. This melts at 243°, is very soluble in water and colors methyl orange red. Titration:

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[1] Ber. d. chem. Ges., **18**, 3172. Cf. Claisen and Roosen Ann. Chem. (Liebig), **278**, 297.

0.2339 gram acid required 10.06 cc. 0.1 N sodium hydroxide solution (phenolphthalein); calculated, 10.11 cc.

The potassium salt seems to contain no water of crystallization. When 1.0417 grams of salt were heated at 140°, during 5 hours, it lost 0.0062 gram of water. When 0.2568 gram of salt was heated at 140°, during 2 hours, it lost 0.0037 gram of water. When a solution of the salt is treated with a solution of silver nitrate no precipitate is formed, but a mirror of silver is deposited on the vessel slowly in the cold and immediately on heating. The salt decolorizes cold potassium permanganate solutions at once, and manganese dioxide is precipitated. Solutions of the salt give no precipitates with barium chloride, lead nitrate, calcium chloride, cobalt nitrate, ferric chloride, copper sulphate (the solution turns pink), mercuric chlorde and mercurous nitrate. Analysis:

0.3971 gram salt, dried at 110°, gave 0.1232 gram K_2SO_4.

0.1527 gram salt, dried at 110°, gave 25 cc. N at 19° (24.2 cc. at 12°) and 627 mm.

	Calculated for $C_7H_8N_3O_4SK$.	Found.
N	15.64	15.51
K	14.53	13.92

α-Carbethoxysemicarbazido-α-isopropionic Nitrile, $NH_2CONHN(COOC_2H_5)CH(CH_3)CN$.—To prepare the α-semicarbazidoisopropionic nitrile,[1] 50 grams of semicarbazide hydrochloride and 29 grams of pure acetic aldehyde ammonia were ground together very intimately for 1 hour. The mixture was put into 250 cc. of pure hydrocyanic acid and allowed to stand 8 days, with frequent agitation. The prussic acid had been slowly distilled twice through a long upward condenser and a second downward condenser connected with the first. Water having a temperature of 27°–28° was run through the first condenser, whereas cold tap water was run through the second condenser. After the reaction was at an end the prussic acid was distilled off, the last portion being removed by a current of air. The residue was extracted with absolute ethyl alcohol in order to dissolve the nitrile and leave the ammonium chloride. The alcoholic extracts gave, upon evaporation, nearly a quantitative yield of α-semicarbazidoisopropionic nitrile, which melted at 124°.

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[1] Bailey and Acree: Ber. d. chem. Ges., **33**, 1524, 1531, 1532.

Three grams of the nitrile were boiled 6 hours, in benzene solution, with 3 grams of ethyl chlorcarbonate in a flask under a return condenser; an oil separated out at the bottom. The benzene was evaporated off and the residue was dissolved in a mixture of alcohol and benzene; when the solvent was allowed to evaporate spontaneously, crystals of the pure α-carbethoxysemicarbazido-α-isopropionic nitrile were formed, which, after crystallizaion from alcohol, melted at 173°. The substance is very soluble in acetone, fairly soluble in ethyl acetate, water and alcohol, and difficultly soluble in chloroform.

The substance was treated with a molecular proportion of barium hydroxide in cold solution to saponify the nitrile and ester groups. The resulting solution was acidified and only by evaporation was the resulting urazole-α-isopropionic acid obtained. This is now under investigation. Analysis:

0.1084 gram substance gave 31.8 cc. N at 16° and 625 mm.

	Calculated for $C_7H_{12}N_4O_3$.	Found.
N	28.06	28.09

o-Hydrazinobenzoic Acid, $NH_2NHC_6H_4COOH$.—This compound was made according to Fisher's method.[1] By diazotizing anthranilic acid and reducing the diazo compound with zinc and acetic acid till the solution is colorless, filtering and then adding hydrochloric acid, a precipitate is formed which is a mixture of the hydrochlorides of anthranilic acid and orthohydrazinobenzoic acid. A sample of the orthohydrazinobenzoic acid hydrochloride was made for us by Kahlbaum and is now listed by him. The sample furnished was found to consist of about 60 per cent anthranilic acid hydrochloride and 40 per cent *o*-hydrazinobenzoic acid hydrochloride. When the mixture of these hydrochlorides was dissolved in a small quantity of water and treated with a saturated solution of a little more than a molecular quantity of sodium acetate, a precipitate was formed at once which the analyses show to be a mixture of the free bases. When this is crystallized twice from alcohol the pure *o*-hydrazinobenzoic acid is obtained. This is sparingly soluble in cold alcohol and in ether, whereas the anthranilic acid is readily soluble in these two liquids. The pure *o*-hydrazinobenzoic acid forms both basic and acid salts. It melts at 249°, probably going over into the anhydride below this temperature. Titration and analyses:

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[1] Ber. d. chem. Ges., 13, 680.

0.1015 gram impure *o*-hydrazinobenzoic acid required 6.87 cc. 0.0994 N potassium hydroxide solution; calculated, 6.71 cc.

I. 0.1147 gram Kahlbaum substance, m. p. 243°, gave 15.15 cc. N, measured over 30 per cent potassium hydroxide at 20° and 772.7 mm.

II. 0.1139 gram Kahlbaum substance, m. p. 243°, gave 15.2 cc. N, measured over 30 per cent potassium hydroxide at 20° and 771.7 mm.

III. 0.1176 gram pure substance, m. p. 249°, gave 19.3 cc. N, measured over 30 per cent potassium hydroxide at 23° and 756.7 mm.

	Calculated for $C_7H_8N_2O_2$.	Calculated for $C_7H_7NO_2$.	Found.		
			I.	II.	III.
N	18.46	10.24	15.23	15.54	18.52

o-Hydrazinobenzoic Acid Hydrochloride.[1]—The sample furnished by Kahlbaum melted at 207° and was mixed with a considerable quantity of a colored substance insoluble in water. The hydrochloride is very soluble in alcohol and in water and when pure is white. Titration and analyses:

0.1000 gram substance required 11.35 cc. 0.907 0.1 N potassium hydroxide solution; calculated, 11.59 cc.

I. 0.1100 gram substance gave 15.5 cc. N, measured over 30 per cent potassium hydroxide solution, at 29°.5 and 759.3 mm.

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[1] Emil Fischer: *loc. cit.*

II. 0.1115 gram substance gave 15.2 cc. N, measured over 30 per cent potassium hydroxide solution, at 24°.8 and 762 mm.

	Calculated for $C_7H_9N_2O_2Cl$.	Found. I.	II.
N	14.92	15.44	15.35

o-Hydrazinobenzoic Acid Hydrobromide.—A sample of the pure hydrazinobenzoic acid was treated with a slight excess of hydrobromic acid solution and evaporated in a desiccator. Needles of the hydrobromide were formed, which melted at 207°–210°. This salt is apparently more soluble in water than the hydrochloride. Titration:

0.1412 gram hydrobromide required 12.25 cc. 0.0994 N potassium hydroxide solution; calculated, 12.25 cc.

α-SemicarbazidoorthobenzoicAcid, $NH_2CONHNHC_6H_4COOH$.—Ten grams of orthohydrazinobenzoic acid hydrochloride were treated with 8 cc. of 33 per cent potassium hydroxide solution and 5 grams of potassium cyanate in 25 cc. of water and the mixture was shaken until the hydrochloride was completely dissolved. The resulting solution was acidified with acetic acid and the α-semicarbazidoorthobenzoic acid precipitated nearly completely. The yield was 8.5 grams. The semicarbazide derivative was also formed when the *o*-hydrazinobenzoic acid hydrochloride was shaken with 2 molecules of potassium cyanate in water until the hydrochloride dissolved completely; the substance precipitated out when sulphuric acid was added. The semicarbazide derivative melts at 225°, is somewhat soluble in water, and is very soluble in alcohol. It titrates against alkali as a monobasic acid, and is reprecipitated unchanged from these solutions when strong acids are added.

A solution of the potassium salt was treated with the molecular amount of silver nitrate in solution. A white silver salt precipitated out, but turned black very soon. A solution of 0.5 gram of the acid, in a slight excess of alkali, was treated with the theoretical amount of 0.1 N potassium permanganate solution. The permanganate solution was decolorized instantly; the manganese dioxide was filtered off and the solution of the azo compound was evaporated to a small volume. When sulphuric acid was added, a precipitate of a red sub stance, which is probably the *o*-benzoic acid azocarbamide, $NH_2CON : NC_6H_4COOH$, was formed. This was very hygroscopic and was not analyzed. Titration and analysis:

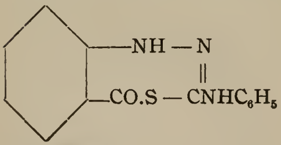
0.1000 gram substance required 5.14 cc. 0.1 N potassium hydroxide solution (phenolphthalein); calculated, 5.13 cc.

0.1825 gram substance gave 33.4 cc. N at 18° and 750 mm.

	Calculated for $C_8H_9N_3O_3$.	Found.
N	21.52	20.82

Potassium δ-Phenylthiosemicarbazido-α-orthobenzoate, $C_6H_4(COOK)NHNHCSNHC_6H_5$.—This compound was made by shaking potassium *o*-hydrazinobenzoate in dilute alcohol, with the equivalent quantity of phenyl mustard oil until the odor of the latter disappeared. When the solution was evaporated to dryness the salt was obtained.

δ-Phenylthiosemicarbazido-α-orthobenzoic Anhydride,



.—When the potassium salt above described was treated with dilute sulphuric acid a precipitate was formed. This was crystallized from alcohol; it then melted at 238°. The substance was neutral and was not changed when evaporated with alkaline solutions, or with lead oxide. Hence the substance must have the sulphur atom in the ring as represented in the formula; any other formula would be that of a substance necessarily soluble in alkalies.

This shows that the α-orthobenzoic acid δ-phenylthiosemicarbazide does not exist except in the form of salts. It loses a molecule of water and forms an anhydride just as

1-phenyl-1-carboxylic acid semicarbazide[1] spontaneously loses a molecule of water and forms phenylurazole. Analysis:

0.1562 gram substance gave 21.6 cc. N at 21° and 754.6 mm.

	Calculated for $C_{14}H_{11}ON_3S$.	Found.
N	15.64	15.60

Johns Hopkins University,
January 1, 1907.

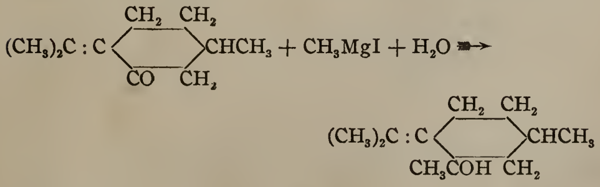
THE REACTION BETWEEN UNSATURATED COMPOUNDS AND ORGANIC MAGNESIUM COMPOUNDS.

XI. CYCLIC KETONES.

By E. P. Kohler.

The experiments described in this paper were performed with the 3 best known types of unsaturated ring ketones, namely: Those which contain unsaturated side chains, those which have an unsaturated nucleus, and those which have 2 ethylene linkages, one of which is in the nucleus, the other in the side chain.

Only one experiment with a ketone of the first type has been described. Grignard[2] added pulegone to methylmagnesium iodide and obtained a hydrocarbon, evidently formed by loss of water from an intermediate tertiary alcohol.



The reaction in this case involved only the carbonyl group but since unsaturated cyclic ketones of this type generally behave like the corresponding open-chain compounds, it seemed probable that this result was due to the presence of the 2 methyl groups in combination with one of the unsaturated carbon atoms. The behavior of dibenzalcyclomethylhexanone confirmed this view. This ketone reacts exactly like dibenzalacetone and gives, ultimately, a mixture of stereoisomeric saturated ketones:

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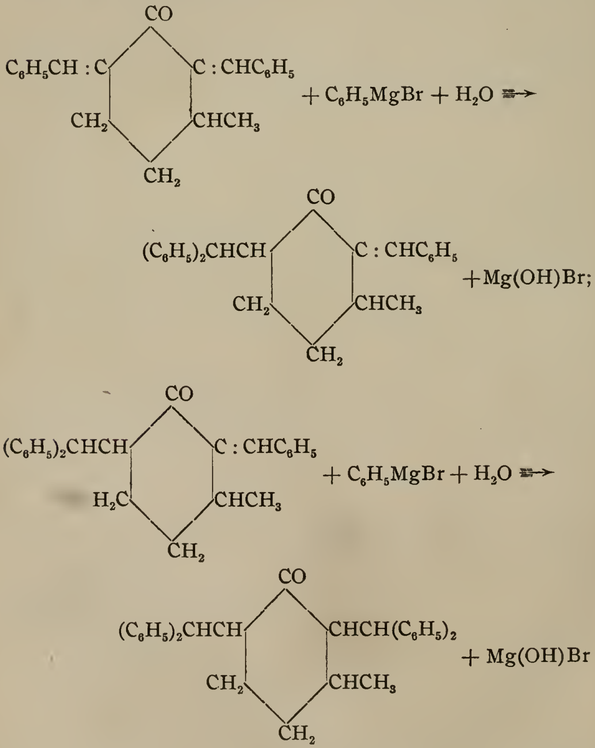
[1] Acree: Ber. d. chem. Ges., 37, 618. Cf. Bailey and Acree: J. Am. Chem. Soc. 26, 1012.

[2] Ann. Chim. Phys. [7], 24, 483.

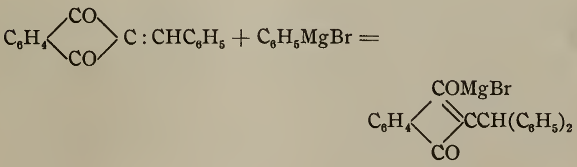


It was possible to prove that these ketones are formed by

1,4-addition. In the last paper[1] it was shown that enols which are formed by 1,4-addition to open-chained unsaturated ketones which have a hydrocarbon residue in the *a*-position are sufficiently stable to permit of transformation into peroxides. This rule appears to hold for the enols obtained from the first type of cyclic ketones. Thus the products obtained from dibenzalcyclomethylhexanone, which is essentially an *a,a*-disubstitution product of dibenzalacetone, were readily transformed into peroxides, while no peroxides could be obtained in experiments with dibenzalacetone.

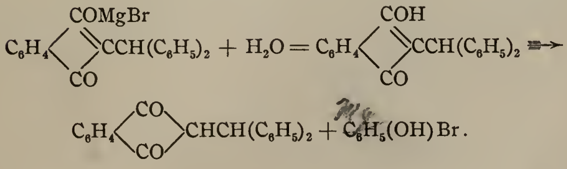
An interesting result was obtained with benzaldiketohydrindene. The reactions to be expected with this substance are represented by the following equations:

I.



$$C_6H_4\left\langle\begin{matrix}CO\\CO\end{matrix}\right\rangle C:CHC_6H_5 + C_6H_5MgBr = C_6H_4\left\langle\begin{matrix}COMgBr\\CO\end{matrix}\right\rangle CCH(C_6H_5)_2$$

II.



$$C_6H_4\left\langle\begin{matrix}COMgBr\\CO\end{matrix}\right\rangle CCH(C_6H_5)_2 + H_2O = C_6H_4\left\langle\begin{matrix}COH\\CO\end{matrix}\right\rangle CCH(C_6H_5)_2 \rightarrow C_6H_4\left\langle\begin{matrix}CO\\CO\end{matrix}\right\rangle CHCH(C_6H_5)_2 + \overset{Mg}{C_6}H_5(OH)Br.$$

The product, however, does not have the composition of the saturated diketone represented, differing from it by 1 molecule of water. Its properties indicate that a new indene ring has been formed, the enol losing water instead of undergoing the usual rearrangement to ketone:

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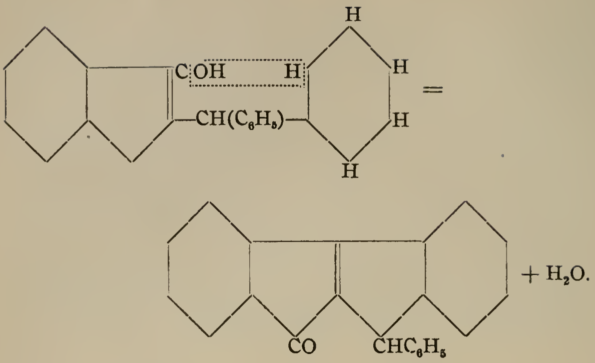
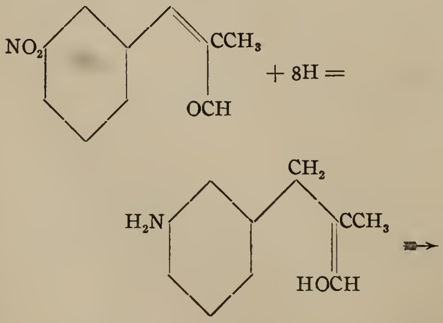
[1] This Journal, 36, 529.



It is probable that a similar process accounts for the peculiarities that have been observed in the formation of simpler indene derivatives from unsaturated compounds. Miller and Rohde[1] found that, while no indene derivative can be obtained by reducing either *α*-methylcinnamic aldehyde or *m*-nitrocinnamic aldehyde, *m*-nitro-*α*-methylcinnamic aldehyde is readily reduced to 2-methyl-6-aminoindene. It is easy to account for these results if we assume that the reduction consists in 1,4-addition of hydrogen:



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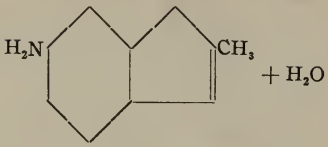
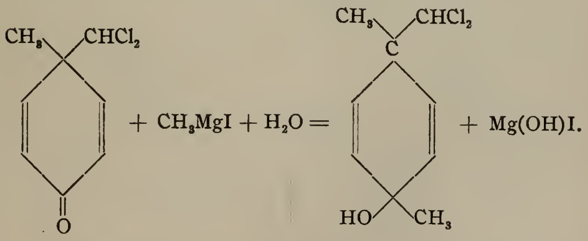
[1] Ber. d. chem. Ges., 22, 1830.



The amino group increases the reactivity of the hydrogen atom in the para position and the methyl group is necessary to impart sufficient stability to the enol[1] and prevent immediate rearrangement to saturated aldehyde.

The reaction between Grignard's reagent and ketones of the second type was first studied by Bamberger and Blangley,[2] who found that toluquinone and xyloquinone give quinoles by addition to the carbonyl group. A little later Auwers and his assistants[3] published results obtained in a very thorough investigation of the reaction with unsaturated cyclic ketones obtained by condensing chloroform with phenols. These also form only 1,2-addition products.



It is clear, from these results, that 1,4-addition products with Grignard's reagent are not obtained with the simplest ketones of this type; but whether a different result would be obtained with ketones in which the reactivity of the carbonyl group is diminished by substituents in the α-position remained to be determined. The most promising substance for this purpose seemed to be carvone. It is easily obtained in any desired quantity, it readily enters into addition reactions that involve the ethylene linkage in the nucleus,[1] and since the substituent in the α-position is a hydrocarbon residue, it was probable that any 1,4-addition that might take place could be recognized by the peroxide reaction. The experiments with carvone were barely finished when papers on the same subject were published by Rupe and Liechtenhan[2] and by Klages and Sommer.[3] My results confirm those published by Rupe and Liechtenhan. When the ketone is added to Grignard's reagent at low temperatures, about 75 per cent of the product is a tertiary alcohol or a hydrocarbon formed from this alcohol and the remainder a new ketone. Rupe and Liechtenhan assume that the ketone is formed by 1,2-addition to the ethylene linkage:

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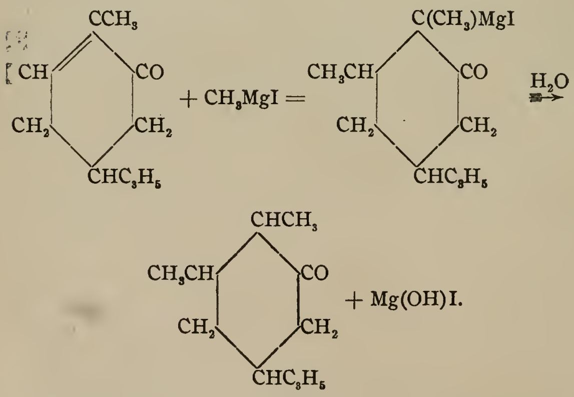
[1] THIS JOURNAL, **36**, 529.

[2] Ber. d. chem. Ges., **36**, 1625.

[3] *Ibid.*, **36**, 1861.



This assumption is certainly wrong. Ketones obtained by the action of Grignard's reagent on unsaturated cyclic ketones are due to 1,4-addition. It is difficult to prove this satisfactorily with carvone, because it is impossible to separate the sensitive substances required for this purpose from the large quantity of indifferent, high-boiling liquids formed at the same time. In the case of diphenylcyclohexanone, however, which gives solid products, the proof is conclusive. This ketone reacts with ethylmagnesium bromide exactly like carvone. If the product is isolated in the usual way, about 80 per cent of it is an unsaturated tertiary alcohol, or a hydrocarbon formed from the alcohol by loss of water—the remainder is a saturated ketone. But if the magnesium derivative is decomposed with sufficient care and the ether evaporated in a current of oxygen, the result is a mixture of tertiary alcohol and enolic peroxide:

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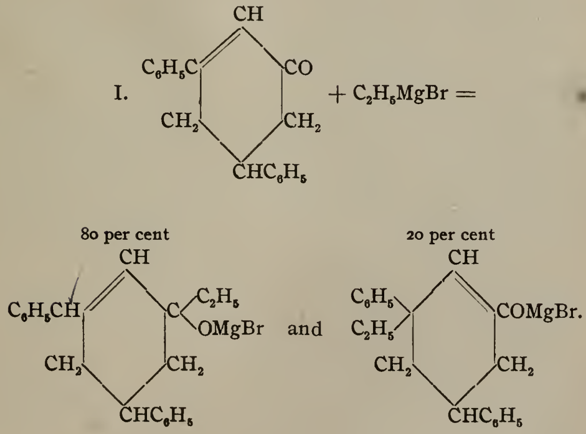
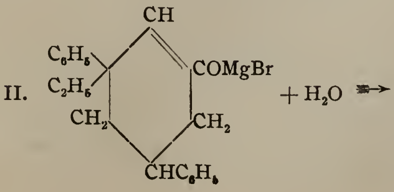
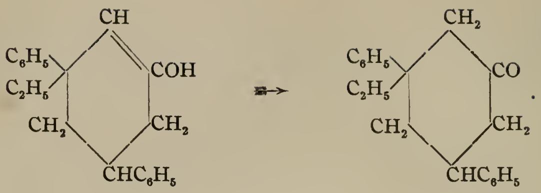
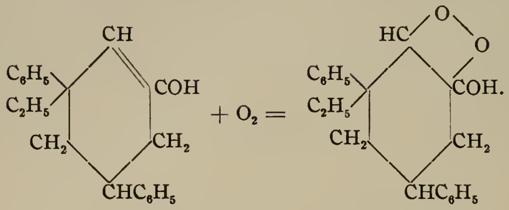
[1] Ber. d. chem. Ges., 37, 4465.
[2] *Ibid.*, 39, 1119.
[3] *Ibid.*, 39, 2306.







III.



It has been pointed out that in open-chained compounds the direction of the reaction sometimes depends upon the magnesium compound that is used. The same is true in the case of diphenylcyclohexanone. With phenylmagnesium bromide the sole product is a tertiary alcohol, formed by 1,2-addition to carbonyl, while with ethylmagnesium bromide the product is a mixture of tertiary alcohol with ketone formed by 1,4-addition. Diphenylcyclohexanone also forms complex products like those obtained from open-chained unsaturated compounds when the organic magnesium compound is not present in sufficient excess. All the results obtained with this type of unsaturated ketone indicate that there is no qualitative difference between their behavior towards Grignard's reagent and that of open-chained unsaturated compounds.

EXPERIMENTAL PART.

Experiments with Dibenzalcyclomethylhexanone.

The ketone used in these experiments was made by introducing 2 benzal groups[1] into methylhexanone obtained from pulegone. When the finely powdered substance is added to excess of ethereal phenylmagnesium bromide it reacts like open-chained unsaturated ketones; the bright red intermediate compound that first forms readily redissolves and the reaction is complete as soon as all the color has disappeared. The product, isolated in the usual way, is a mixture that can be separated by repeated crystallization from chloroform and absolute alcohol. The least soluble substance obtained crystallizes from chloroform in hard needles, melting at 192°. It is readily soluble in chloroform and benzene, moderately in acetone and ethyl acetate, sparingly in boiling absolute alcohol and ether. A more soluble product accumulated in the mother liquors. This separated from absolute alcohol in long, fine needles melting at 132°. It is readily soluble in chloroform, acetone and absolute alcohol. The combined filtrates from these compounds slowly deposited long needles, melting at 154°–156°, but this third product was not obtained in sufficient quantity for analysis:

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[1] Ber. d. chem. Ges., 29, 1597.

I. 0.1337 gram substance (192°) gave 0.4340 gram CO_2 and 0.0866 gram H_2O.

II. 0.1604 gram substance (132°) gave 0.5200 gram CO_2 and 0.1071 gram H_2O.

	Calculated for $C_{27}H_{26}O$.	Found. I.	II.
C	88.52	88.50	88.32
H	7.10	7.11	7.21

Both of these substances dissolve in concentrated sulphuric acid and give orange-colored solutions; both decolorize a solution of bromine in chloroform and reduce potassium permanganate dissolved in acetone. The analytical results show that the substances are isomeric and the behavior towards phenylmagnesium bromide described below proves that they are ketones. As the original ketone is unsymmetrical and the product contains 2 asymmetric carbon atoms, both structural and spatial isomerism is possible, and the location of the benzal and diphenylmethyl groups is uncertain.

Peroxides.—When a rapid current of oxygen was passed through the ethereal solution obtained by decomposing the magnesium derivatives from dibenzalmethylcyclohexanone, with iced hydrochloric acid, the result was a mixture of peroxides quite free from ketones. It was extremely difficult to get a pure substance from this mixture of sensitive compounds. The best results were obtained by solution in chloroform, followed by very slow precipitation with ligroin. After many repetitions of this operation two compounds melting at 176° and 142° were finally obtained in quantities sufficient for analysis. Both substances crystallized in colorless needles and decomposed a few degrees above the melting point.

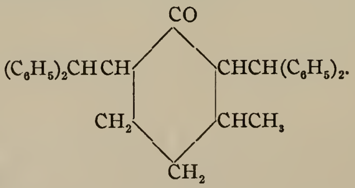
Analysis:

I. 0.1420 gram substance (176°) gave 0.4248 gram CO_2 and 0.0868 gram H_2O.

II. 0.12279 gram substance (142°) gave 0.3830 gram CO_2 and 0.0786 gram H_2O.

	Calculated for $C_{27}H_{26}O_3$.	Found. I.	Found. II.
C	81.41	81.58	81.66
H	6.53	6.78	6.82

Tetraphenyltrimethylcyclohexanone,



—The 2 isomeric ketones described above react with ethereal phenylmagnesium bromide at the ordinary temperature, and both give the same products. The ethereal solution obtained by decomposing the magnesium derivatives was allowed to stand in a closed separating funnel for several days, then filtered and the filtrate evaporated to small volumes. The solid that separated in the funnel was purified by recrystallization from benzene, which deposited it in fine needles, melting at 282°. The substance is almost insoluble in boiling absolute alcohol, sparingly in boiling acetone and chloroform, moderately in hot benzene. A second product separated from the filtrates. This was purified by recrystallization from absolute alcohol. It separated in long, silky needles melting at 190°; readily soluble in alcohol, ether and chloroform.

Analyses:

I. 0.1227 gram substance (282°) gave 0.4010 gram CO_2 and 0.0790 gram H_2O.

II. 0.1214 gram substance (190°) gave 0.3961 gram CO_2 and 0.0758 gram H_2O.

	Calculated for $C_{33}H_{32}O$.	Found. I.	II.
C	89.18	89.03	88.98
H	7.21	7.14	6.94

The analyses show that the substances are isomeric. Tests with an acetone solution of potassium permanganate indicated that both are saturated and tests with ethylmagnesium bromide proved the absence of hydroxyl groups. The substances are, therefore, saturated ketones and, since structural isomerism is impossible, they are, doubtless, stereoisomers. It is noteworthy that neither of the ketones reacts with phenylmagnesium bromide in boiling ethereal solution, the groups around the carbonyl interfering with the reaction in the same way that they do in benzpinacolin and similar compounds.

Experiments with Benzaldiketohydrindene.

The ketone was made by heating diketohydrindene with excess of benzaldehyde[1] to 120°. The product was ground up with absolute alcohol, filtered and recrystallized from ethyl acetate. When the finely powdered solid is added, in very small portions, to ethereal phenylmagnesium bromide it first imparts a brilliant red color to the solution, then produces a permanent red precipitate. This precipitate interferes with the reaction because it protects the sparingly soluble ketone from the reagent. The most satisfactory procedure was as follows: A solution of the ketone in boiling benzene was added, in small portions, to a boiling solution of the reagent and the resulting dark red liquid boiled for an hour to complete the reaction. The magnesium derivative was decomposed with iced acid, the yellow benzene-ether layer removed and distilled with steam until diphenyl could no longer be detected in the distillate. The orange-colored residue was washed with a small quantity of cold alcohol, then dissolved in boiling absolute alcohol. The substance separated in quinone-yellow plates, melting at 162°.

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[1] Ann. Chem. (Liebig), 252, 75.

Analyses:

I. 0.1410 gram substance gave 0.4665 gram CO_2 and 0.0630 gram H_2O.

II. 0.1188 gram substance gave 0.3923 gram CO_2 and 0.0538 gram H_2O.

	Calculated for $C_{22}H_{14}O$.	Found.	
		I.	II.
C	89.95	90.23	90.08
H	4.76	5.04	5.03

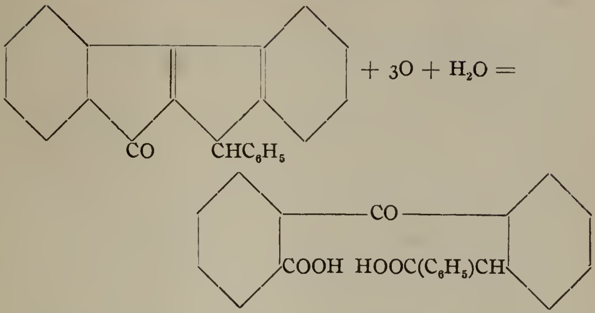
The substance is readily soluble in chloroform, moderately in acetone and ethyl acetate, sparingly in alcohol. Concentrated sulphuric acid first turns it red, then dissolves it, forming a dark green solution. In acetone solution it readily reduces potassium permanganate. The principal oxidation product is an acid. This was purified by recrystallization from a mixture of ether and low-boiling ligroin. It was deposited in aggregates of flat, colorless needles, melting at 131°–133°. It is very readily soluble in alcohol and ether, sparingly soluble in ligroin.

Analysis:

0.1238 gram substance gave 0.3341 gram CO_2 and 0.0500 gram H_2O.

	Calculated for $C_{22}H_{16}O_5$.	Found.
C	73.33	73.44
H	4.44	4.48

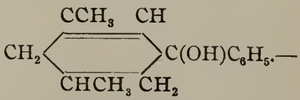
The formation of this acid establishes the formula of the ketone. The oxidation is represented by the equation:



A convenient name for a hydrocarbon with the carbon skeleton contained in the ketone would be "bindene." The ketone itself would then be 6-phenylbindenone-8.

Experiments with Dimethylcyclohexenone and Benzaldimethylcyclohexenone.

Phenyldimethylcyclohexenol,



$$\mathrm{CH_2}\Big\langle\overset{\mathrm{CCH_3}\quad\mathrm{CH}}{\underset{\mathrm{CHCH_3}\;\;\mathrm{CH_2}}{\overline{\qquad\qquad\qquad}}}\Big\rangle\mathrm{C(OH)C_6H_5}.—$$

Knoevenagel and Lange[1] found that when hydrocyanic acid combines with dimethylcyclohexenone, the addition takes place at the ethylene linkage and the product is a saturated ketone. The following experiment shows that when phenylmagnesium bromide combines with the same ketone the addition is to carbonyl and the product is a tertiary alcohol. Twenty-five grams of the ketone were added slowly to a well cooled solution of phenylmagnesium bromide and the mixture allowed to stand for 10 hours. The resulting magnesium derivative was decomposed in the usual way and the ethereal solution allowed to evaporate. The product separated in large, colorless plates. After one crystallization from a mixture of ether and low-boiling ligroin the substance melted sharply at 111°. The yield of pure product was 36 grams.

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[1] Ber. d. chem. Ges., 37, 407.

Analysis:

0.1385 gram substance gave 0.4240 gram CO_2 and 0.1140 gram H_2O.

	Calculated for $C_{14}H_{18}O$.	Found.
C	83.2	83.48
H	8.9	9.14

For the purpose of distinguishing between ketone and tertiary alcohol an ethereal solution containing 5 grams of the substance was added to excess of ethylmagnesium bromide. The reaction was accompanied by a steady evolution of gas and 4.4 grams of the original substance was recovered when the magnesium derivative was decomposed with ice and acid. The product is, therefore, a tertiary alcohol. It is readily soluble in all organic solvents except ligroin, combines with bromine and reduces potassium permanganate at the ordinary temperature.

Benzaldimethylcyclohexenone.—Knoevenagel and Klages[1] condensed benzaldehyde and dimethylcyclohexenone in the presence of a large quantity of very dilute alcohol. The following procedure is more satisfactory because it can be completed in much shorter time and yields a purer product. A mixture of 50 grams of benzaldehyde and the same weight of ketone is diluted with an equal volume of alcohol. This solution is cooled with ice-water, then treated with 20 grams of a 10 per cent solution of sodium hydroxide and placed in an ice chest. In the course of an hour or two the liquid separates into 2 layers. A speck of solid ketone, added at this stage, induces a slow crystallization of almost pure product. The mixture is allowed to remain in the ice chest for 8 hours, then filtered, the solid washed with alcohol and water, and purified by recrystallization from alcohol. From the filtrate, which is returned to the ice chest, a considerable quantity of less pure product separates in the course of 24 hours. The total yield of pure substance is from 70 to 75 per cent of the calculated amount.

When dibenzaldimethylcyclohexenone is added to ethereal phenylmagnesium bromide it produces the usual intermediate colored precipitate. This slowly dissolves on shaking and gives rise to a voluminous, colorless precipitate that interferes with the reaction by protecting the intermediate compound from further action of the reagent. It is necessary, therefore, to use a large excess of the reagent and to boil the mixture until all trace of color has disappeared. It is requisite, also, to decompose the magnesium compound at as low a temperature as possible, otherwise the result is an oil that does not solidify in a freezing mixture and does not distil under diminished pressure without decomposition. If the magnesium derivative is poured, slowly, into a freezing mixture of ice and concentrated hydrochloric acid and the ethereal layer first washed with ice water and then diluted with low-boiling ligroin, the product is a colorless solid. The impure solid slowly passes into oil, but it can be purified with slight loss by recrystallization from ether, and the pure substance is stable at the ordinary temperature. It crystallizes in large, lustrous tables, is readily soluble in organic solvents except ligroin and melts at 106°.

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[1] Ann. Chem. (Liebig), 281, 118.

Analysis:

I. 0.1365 gram substance gave 0.4110 gram CO_2 and 0.0995 gram H_2O.

II. 0.1262 gram substance gave 0.3775 gram CO_2 and 0.5930 gram H_2O.

	Calculated for $C_{21}H_{24}O_2$.	Found.	
		I.	II.
C	81.82	82.11	81.61
H	7.79	8.09	8.11

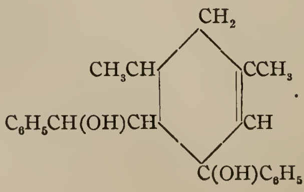
A product formed by the addition of a molecule of ethylmagnesium bromide to benzaldimethylcyclohexenone would have the formula $C_{21}H_{22}O$; the substance differs from this by 1 molecule of water, which is probably added when the magnesium derivative is decomposed.

The behavior of the substance towards ethylmagnesium bromide shows that it, in all probability, contains 2 hydroxyl groups. Twelve grams (1 mol.) were added to a solution of ethylmagnesium bromide made from 1 gram—

slightly more than 2 atoms—of magnesium. Effervescence stopped before quite all of the solid had been introduced and there was no evolution of gas when the magnesium derivative was decomposed with iced acid. The magnesium compound appeared to be the same that was obtained in the original reaction. When decomposed, it gave a little over 10 grams of the substance melting at 106°. The product, therefore, reacts with 2 molecules of ethylmagnesium bromide, but no addition takes place, indicating the absence of carbonyl and the presence of 2 hydroxyl groups.

The substance readily reduced potassium permanganate dissolved in acetone. The acetone, on evaporation at the ordinary temperature, left only a minute quantity of oil, showing that there are no neutral oxidation products. The salts were dissolved in water, the solution acidified and the acids extracted with ether. The ether, on evaporation, left an oil that partially solidified in a freezing mixture. By exhaustive extraction with cold, low-boiling ligroin it was possible to remove all of the solid without dissolving more than a trace of oil. The ligroin, on evaporation, left almost pure benzoic acid. Thirteen grams of substance gave 6.4 grams of benzoic acid—almost exactly 1 molecule for 1 of the substance.

It has not been possible, thus far, to get either the oily acid or any of its derivatives sufficiently pure for analysis. Nor has it been possible to find any other reaction that would give more definite information as to the nature of the product $C_{21}H_{24}O_2$. Its structure is, therefore, uncertain, but the most probable formula is



Experiments with Diphenylcyclohexenone.

(In Part by Mary Violet Dover.)

Most of the unsaturated ketone used in the following experiments was made according to directions by Knoevenagel and Schmidt.[1] As this method does not give a satisfactory yield we tried the condensation at low temperatures and in the presence of a small quantity, instead of 1 equivalent, of sodium alcoholate. We found that, under these conditions, the reaction consists in the addition of a molecule of acetoacetic ester to one of benzalacetophenone, just as it does when diethylamine is used as a condensing agent. The differences observed by Knoevenagel[2] when he used sodium alcoholate and diethylamine for bringing about the same reaction are, therefore, not to be ascribed to the specific properties of the condensing agent, but to the differences in the amounts of these agents used and to the temperatures at which the condensations were effected.

The addition product obtained when sodium alcoholate is used is, however, not identical but isomeric with that obtained with diethylamine. The procedure was as follows: A solution of 0.5 gram of sodium, in a little absolute alcohol, was added to 30 grams of benzalacetophenone and 15 grams of acetoacetic ester, dissolved in 100 cc. of absolute alcohol, and the mixture placed in an ice chest. Long white needles of the product began to separate in a short time and the condensation was complete in 24 hours. The solid was purified by means of alcohol. It is readily soluble in boiling alcohol, sparingly soluble in cold alcohol and in ether. It crystallizes in colorless needles, melting at 168°. In agreement with Knoevenagel we found that the product obtained when diethylamine is used as condensing agent melts at 121°.

Analysis:

0.1652 gram substance gave 0.4520 gram CO_2 and 0.0946 gram H_2O.

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[1] Ann. Chem. (Liebig), **281**, 59.

[2] Ber. d. chem. Ges., **35**, 397.

	Calculated for $C_{21}H_{22}O_4$.	Found.
C	74.55	74.63
H	6.50	6.35

Thirty grams of benzalacetophenone gave 34.5 grams of pure product. The substance is evidently closely related to that obtained by using diethylamine, as both give the same cyclic ester when heated with sodium alcoholate. As the product is a β-ketonic ester containing 2 unequal, asymmetric carbon atoms, the 2 substances may be either structural or spatial isomers. There is no advantage in carrying out the reaction in steps, as the loss of material takes place during the closing of the ring. These 4 grams of the substance, boiled for an hour with 0.4 gram sodium, dissolved in 25 cc. of absolute alcohol, yielded only 2.7 grams of diphenylcarboxethylcyclohexenone, melting at 111°.

The ketone that we obtained by hydrolyzing the cyclic ester, as directed by Knoevenagel and Schmidt and recrystallizing the product from alcohol, had a considerably higher melting point than that given by these authors —83° instead of 70°–72°. That it was pure diphenylketocyclohexenone is shown by the following analysis:

0.2016 gram substance gave 0.6434 gram CO_2 and 0.1196 gram H_2O.

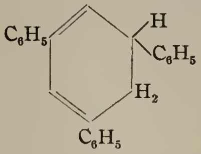
	Calculated for $C_{18}H_{16}O$.	Found.
C	87.1	87.00
H	6.4	6.54

For the purpose of future identification, we made the oxime by heating an alcoholic solution of the ketone with hydroxylamine hydrochloride and powdered sodium carbonate. The oxime crystallizes in needles, melting at 163°–164°, is readily soluble in alcohol, sparingly in ether, insoluble in water.

Analysis:

0.1367 gram substance gave 0.5088 gram CO_2 and 0.0989 gram H_2O.

	Calculated for $C_{18}H_{17}ON$.	Found.
C	82.13	81.8
H	6.3	6.42

Reaction with Phenylmagnesium Bromide: Triphenyldihydrobenzene,  .—The finely powdered ketone was added, gradually, to excess of phenylmagnesium bromide and the mixture allowed to stand for 12 hours. The new magnesium derivative separated in the form of colorless crystals. It was decomposed with iced acid, the ethereal layer evaporated and the solid residue recrystallized from alcohol.

0.1608 gram substance gave 0.5508 gram CO_2 and 0.0947 gram H_2O.

	Calculated for $C_{24}H_{20}$.	Found.
C	93.5	93.40
H	6.5	6.52

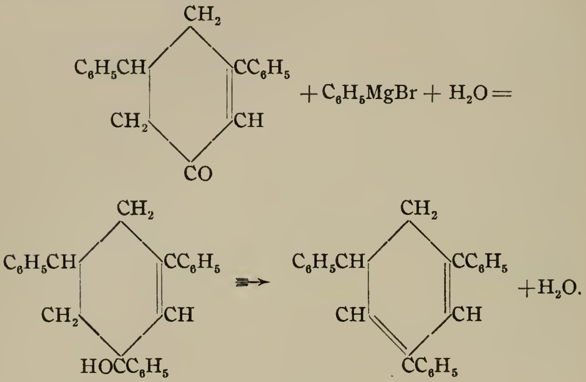
The substance is a hydrocarbon, evidently formed by loss of water from a tertiary alcohol. It readily reduced a solution of potassium permanganate at the ordinary temperature, the sole product of oxidation being another hydrocarbon which, after crystallization from chloroform, melted at 172°.

Analysis:

0.1572 gram substance gave 0.5461 gram CO_2 and 0.0856 gram H_2O.

	Calculated for $C_{24}H_{18}$.	Found.
C	94.1	94.07
H	5.9	6.04

The oxidation product has the composition and almost the melting point given for 1,3,5-triphenylbenzene. It was completely identified by comparison with a specimen of *sym*triphenylbenzene, made by condensing acetophenone. The product of the reaction with phenylmagnesium bromide is, therefore, triphenyldihydrobenzene:



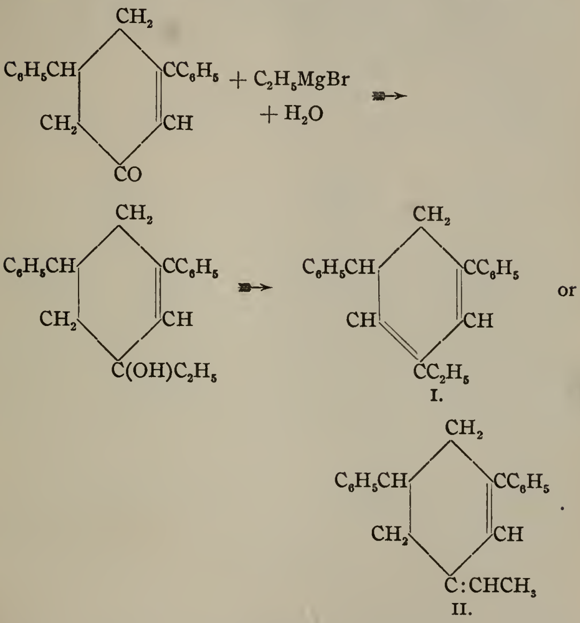
Triphenyldihydrobenzene crystallizes in colorless needles that melt at 111°. It is readily soluble in acetone and chloroform, moderately in alcohol and ether. The yield of pure product was 87 per cent of the calculated quantity.

Reaction with Ethylmagnesium Bromide.—The procedure was the same as that described under phenylmagnesium bromide. The product, isolated in the usual way, was an oil that was evidently a mixture. By repeated distillation under diminished pressure it was separated into 2 fractions, the one boiling at 152° (22 mm.), the other 153°–158° (22 mm.). The fraction boiling at 152° gave the following analytical results:

0.1331 gram substance gave 0.4492 gram CO_2 and 0.0934 gram H_2O.

	Calculated for $C_{24}H_{20}$.	Found.
C	93.2	93.04
H	7.7	7.79

There are only 2 possible formulas for this hydrocarbon:



For the purpose of distinguishing between these formulas the hydrocarbon was oxidized with potassium permanganate, dissolved in acetone. The product was an acid, melting at 155°–157°.

Analysis:

0.1337 gram substance gave 0.3712 gram CO_2 and 0.0696 gram H_2O.

	Calculated for $C_{17}H_{16}O_3$.	Found.
C	76.1	75.7
H	6.0	5.8

As it was difficult to get an acid with a perfectly sharp melting point we confirmed the formula by an analysis of the methyl ester, obtained by saturating a methyl alcoholic solution of the acid with hydrogen chloride. The ester crystallized in stout needles, melting at 94°.

Analysis:

0.1260 gram substance gave 0.3527 gram CO_2 and 0.0730 gram H_2O.

	Calculated for $C_{18}H_{18}O_3$.	Found.
C	76.6	76.26
H	6.4	6.42

A hydrocarbon with the structure represented by I. might be oxidized either to ethyldiphenylbenzene or to α-phenyl-β-benzoylpropionic acid, while a hydrocarbon with the structure represented by II. would be expected to give β-phenyl-γ-benzoylbutyric acid. We made the latter in accordance with the directions given by Vorländer and Knotsch and identified both our acid and its methyl ester. The hydrocarbon is, therefore, ethylidenediphenyltetrahydrobenzene.

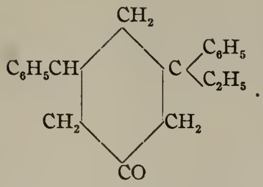
The fraction boiling at 152°–168° was a mixture of the hydrocarbon just described and a substance indifferent to potassium permanganate. As it could not be completely separated it was oxidized in solution in acetone. The hydrocarbon was destroyed, the resulting potassium salt being deposited with the oxides of manganese, while the indifferent compound remained in solution. By evaporating the acetone and distilling the oily residue under diminished pressure, the substance was obtained in pure condition—a colorless oil boiling at 170° (24 mm.).

Analysis:

0.1313 gram substance gave 0.4142 gram CO_2 and 0.0963 gram H_2O.

	Calculated for $C_{20}H_{22}O$.	Found.
C	86.33	86.03
H	7.94	8.15

The indifference to permanganate shows that this substance is the saturated ketone—ethyldiphenylcyclohexanone,



In order to determine whether the ketone was formed by direct addition to the ethylene linkage, or by 1,4-addition, the reaction with ethylmagnesium bromide was repeated, but instead of allowing the ethereal solution to stand it was immediately evaporated in a rapid stream of oxygen. The residue partially solidified in a freezing mixture. The oil was removed, the solid washed with ligroin and repeatedly recrystallized from a mixture of chloroform and ether. It was thus obtained in small, hard prisms, melting, with decomposition, at 269°–270°; sparingly soluble in alcohol and ether, moderately in acetone; readily in chloroform.

Analysis:

0.1269 gram substance gave 0.3615 gram CO_2 and 0.0845 gram H_2O.

	Calculated for $C_{20}H_{22}O_3$.	Found.
C	77.4	77.69
H	7.01	7.39

The substance is ethyldiphenylcyclohexenol peroxide, as represented in the introduction. Its production proves that when ketones are formed by the action of Grignard's reagent on unsaturated cyclic ketones the result is due to 1,4-addition.

The above-mentioned products—hydrocarbon and ketone—were obtained by using a large excess of ethylmagnesium bromide. When unsaturated ketone and magnesium derivatives are used in equivalent quantities the result is somewhat different. The same hydrocarbon is produced, in approximately the same amount, but in place of the ketone there is a complex product quite similar to the substances obtained from open-chained unsaturated ketones. The product separated in the solid form when the magnesium derivatives were decomposed with iced acid. It was purified by recrystallization from chloroform and was deposited in fine needles, melting at 256°.

Analysis:

0.1441 gram substance gave 0.4560 gram CO_2 and 0.0972 gram H_2O.

	Calculated for $C_{38}H_{38}O_2$.	Found.
C	86.69	88.30
H	7.22	7.51

The composition indicates that the substance is formed by the addition of a molecule of unsaturated ketone to the primary product, but not much reliance can be placed on conclusions drawn from the analytical results obtained from these complex substances.

CHEMICAL LABORATORY,
BRYN MAWR COLLEGE.

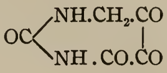
Contributions from the Sheffield Laboratory of Yale University.

CXLII.—RESEARCHES ON PYRIMIDINES: SYNTHESIS OF URACIL-5-CARBOXYLIC ACID.

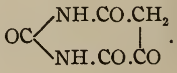
[NINETEENTH PAPER.]

BY HENRY L. WHEELER, TREAT B. JOHNSON, AND CARL O. JOHNS.

A new substance, having acid properties, called orotic acid (*Acido orotico*) has been isolated by Biscaro and Belloni[1] from milk. They assign to this compound the empirical formula, $C_5H_4O_4N_2.H_2O$, and believe that its structure is to be represented by one of the following formulas:



$$OC\begin{cases}NH.CH_2.CO \\ NH.CO.CO\end{cases}$$



$$OC\begin{cases}NH.CO.CH_2 \\ NH.CO.CO\end{cases}.$$

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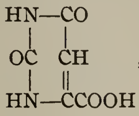
[1] Annuario della Soc. Chimica di Milano, XI, fasc. I (1905); *Ibid.*, XI, fasc. II (1905) *Vide* also Centrabl., 1905, I, 63, 64. We take this occasion to thank the above authors for sending us reprints of these two articles.

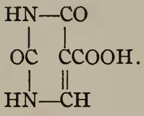
It seemed to us that instead of a ring with 7 members, one with 5 or 6 would most probably prove to be correct. The properties of the substance and the fact that it gives urea on oxidation, suggested that it might be a pyrimidine.

The above empirical formula is that of a uracil carboxylic acid having a molecule of water of crystallization. There are 2 uracil carboxylic acids which have the acid group attached to carbon, namely, the 4- (I.) and 5- (II.) derivatives,



$$\begin{array}{ll}\mathrm{HN}- & \mathrm{CO}\\ | & | \\ \mathrm{OC} & \mathrm{CH} \\ | & \| \\ \mathrm{HN}- & \mathrm{CCOOH}\end{array},$$

I.



$$\begin{array}{ll}\mathrm{HN}- & \mathrm{CO}\\ | & | \\ \mathrm{OC} & \mathrm{CCOOH.} \\ | & \| \\ \mathrm{HN}- & \mathrm{CH}\end{array}$$

II.

As neither of these acids have hitherto been prepared, a description is now given of the preparation and properties of the latter acid, while an account of uracil-4-carboxylic acid will appear in a later article. The study of these acids, and also the carboxyl derivatives of thymine and cytosine, is of interest on account of the possibility that in the nucleic acids uracil, thymine and cytosine may exist as carboxyl derivatives, being held together not alone by means of phosphorus atoms, as suggested by Bang[1] and Osborne and Harris,[2] but also by an acid amide or polypeptide grouping as in the case of the proteids. In such an event the means hitherto used to disrupt the nucleic acid molecule must also cause a loss of the carboxyl group from the pyrimidines. In this connection it is interesting to note that uracil-4-carboxylic acid can be heated with 20 per cent sulphuric acid, at 160°–170°, without alteration while, by such treatment, uracil-5-carboxylic acid is quantitatively converted into uracil. In fact, simply on prolonged boiling of this acid with hydrochloric acid it is converted into uracil. Uracil may, therefore, exist in the nucleic acids as a 5-carboxyl compound. We have shown that the pseudothioureas, $H_2NC(SR) : NH$, will react with aldehyde[3] and ketone esters to form pyrimidines in cases where urea refuses to act. According to Behrend the alkyl acetoacetic esters do not condense with urea.[1] We found that the methyl and ethyl derivatives give pyrimidines with the pseudothioureas. In that article we described 4,5-dimethyluracil as new, having missed the fact that Schlenker had obtained this substance by a different method.[2]

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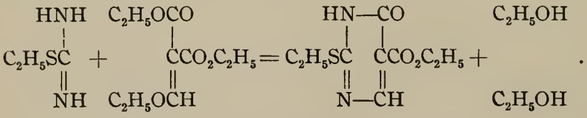
[1] Z. physiol. Chem., 31, 425 (1900).

[2] Conn. Exper. Sta. Rep., 1901, p. 418.

[3] THIS JOURNAL, 29, 480 (1903).

Another striking example of the difference between urea and a pseudothiourea was found when we tried the behavior of Claisen's ethoxymethylenemalonic ester[3] toward these compounds. Urea showed no sign of reacting at 140° and a condensation was not effected on standing in alkaline solutions.

On the other hand, when ethoxymethylenemalonic ester was added to an alkaline, aqueous solution of ethylpseudothiourea hydrobromide,[4] an immediate reaction took place and a salt of 2-ethylmercapto-5-carbethoxy-6-oxypyrimidine separated. This condensation can be represented as follows:



$$\begin{matrix} HNH & C_2H_5OCO & & HN-CO & & C_2H_5OH \\ | & | & & |\quad | & & \\ C_2H_5SC \; + & CCO_2C_2H_5 & = & C_2H_5SC \;\; CCO_2C_2H_5 & + & \\ \| & \| & & \|\quad \| & & \\ NH & C_2H_5OCH & & N-CH & & C_2H_5OH \end{matrix} .$$

2-Ethylmercapto-5-carbethoxy-6-oxypyrimidine (I. see below) can be converted directly into uracil-5-carboxylic acid (IV.) by simply boiling with aqueous hydrochloric acid. When the mercapto ester (I.) is boiled, in alcoholic solution, with a small quantity of hydrochloric acid, uracil-5-ethylcarboxylate (II.) results. And this, on saponification, gives uracil-5-carboxylic acid. On the other hand, warm alkalies saponify the mercapto ester (I.) and give 2-ethylmercapto-5-carboxyl-6-oxypyrimidine (III.), which, with hot hydrochloric acid, gives uracil-5-carboxylic acid (IV.). When the acid (IV.) is melted it gives uracil (VI.).

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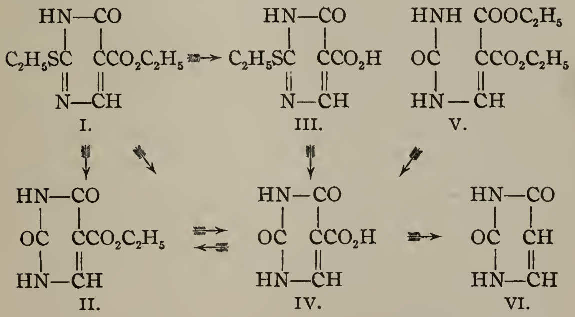
[1] Ann. Chem. (Liebig), **229**, 16 (1885).

[2] Ber. d. chem. Ges., **34**, 2812 (1901).

[3] Ann. Chem. (Liebig), **297**, 75 (1897).

[4] This Journal, **29**, 483 (1903).

The formation of uracil, in this manner and also on heating with acids, shows that the condensation took place as represented in the above equation and that the product (I.) is not a barbituric acid derivative. In fact, we have not yet observed a satisfactory condensation of malonic ester, or any of its derivatives, with the pseudothioureas to form barbituric acid derivatives. The substance represented by Formula V., uramidomethylenmalonic ester, was occasionally found as a by-product in the mother liquors of the condensation. On saponification it gave uracil-5-carboxylic acid. These compounds and their transformations can be represented as follows:



In some respects the properties of uracil-5-carboxylic acid agree closely with those of orotic acid. It is difficultly soluin water, difficultly or insoluble in organic solvents and it crystallizes with the required 1 molecule of water of crystallization. Orotic acid is said to decompose at 260°. Our acid melts, with decomposition, at 278°. The potassium salt that crystallizes from solutions containing an excess of alkali is a monopotassium salt, $C_5H_3O_4N_2K$. Like orotic acid, our acid is dibasic and forms 2 series of salts. The potassium salt gives precipitates with barium chloride (crystalline), lead acetate and silver nitrate.

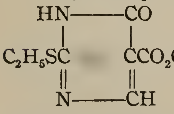
On the other hand, uracil-5-carboxylic acid differs from orotic acid as follows: It does not give a monosilver salt having the composition $C_5H_3O_4N_2Ag.H_2O$, which Biscaro and Belloni state is formed when silver nitrate is added to a solution of the monopotassium salt. In our case, when the monopotassium salt or alkali, acid and silver nitrate, in the proportion 1 : 1 : 1 were used, the silver salt formed was a disilver salt, a corresponding amount of acid remaining in the filtrate.

When methyl iodide was allowed to react, under pressure, on either mono or disilver orotate, Biscaro and Belloni obtained a monomethyl derivative melting at 248°–250°. When we heated our silver salt with methyl iodide, in a closed tube at 100°, we obtained a mixture of substances from which a dimethyl derivative, melting about 254°–256°, was isolated. Their monoethyl ester melted at 200°; our product, obtained in like manner from the silver salt, melted at 162°–163, and the analysis showed that it was a diethyl derivative.

The free uracil-5-carboxylic acid does not give a precipitate with barium chloride, and we were unable to obtain a dichloride, which could be crystallized from boiling water without reverting to the acid, when the potassium salt was heated with phosphorus oxychloride.

EXPERIMENTAL PART.

2-Ethylmercapto-5-carbethoxy-6-oxypyrimidine,



.—The best results in the preparation of this substance were obtained as follows: Fifty-four grams of ethoxymethylenemalonic ester were added to a solution of 50 grams of ethylpseudothiourea hydrobromide in 50 cc. of water. To this mixture 30 grams of potassium hydroxide were slowly added and the solution was kept cold. The addition of alkali produced a yellow color and the solution became semisolid from the separation of a bulky, yellow precipitate. This impure potassium salt, when dry, weighed 58 grams, the yield being 87 per cent of the calculated, theory requiring 66.5 grams. It crystallized from water in the form of colorless prisms and from alcohol in needles.

When a strong aqueous solution of the potassium salt was treated with dilute hydrochloric acid, avoiding an excess of acid, 2-ethylmercapto-5-carbethoxy-6-oxypyrimidine separated as a white, crystalline precipitate. This substance is readily soluble in hot alcohol and it separates in the form of long, slender, colorless prisms; from water it forms long, bulky, asbestos-like needles. It melts at 131° to a clear oil and it gave the following results on analysis (Kjeldahl):

	Calculated for $C_9H_{12}O_3N_2S$.	Found. I.	II.
N	12.23	12.02	12.28

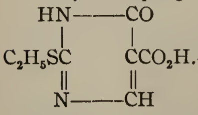
This ester dissolves in cold hydrochloric acid and is reprecipitated by ammonia. It has both acid and basic properties.

Uramidomethylenemalonic Ester, $H_2NCONHCH : C(CO_2C_2H_5)_2$.—This substance was obtained, in 2 experiments, by precipitating with hydrochloric acid, the filtrate from which the potassium salt of 2-ethylmercapto-5-carbethoxy-6-oxypyrimidine had separated. In the above case the amount obtained was 4.8 grams. It is very difficultly soluble in boiling water, readily soluble in hot alcohol; when crystallized from 50 per cent alcohol it forms bunches of colorless prisms melting at 206°, with effervescence. Nitrogen determinations gave (Kjeldahl):

	Calculated for $C_9H_{14}O_5N_2$.	Found. I.	II.
N	12.17	12.22	12.06

This material has acid properties. When warmed with alkali, saponification takes place and hydrochloric acid then precipitates uracil-5-carboxylic acid.

2-Ethylmercapto-5-carboxyl-6-oxypyrimidine,



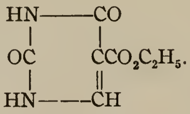
$$\begin{array}{lcl} \text{HN} & \text{——} & \text{CO} \\ | & & | \\ C_2H_5SC & & CCO_2H \\ \| & & \| \\ \text{N} & \text{——} & \text{CH} \end{array}$$

.—Ten grams of the potassium salt of 2-ethylmercapto-5-carbethoxy-6-oxypyrimidine were dissolved in hot alcohol and a hot solution of 4.3 grams of potassium hydroxide, in a little water, were added. Saponification took place immediately and the solution became a thick jelly. The alcohol was then evaporated and the residue taken up in a little water. On adding an excess of hydrochloric acid a white precipitate of the mercapto acid separated. It weighed 7.1 grams, while the calculated is 7.5 grams, the yield being 94.6 per cent of theory.

This acid dissolves readily in hot alcohol, less readily in hot water, from which solvent it forms bunches of colorless, sharp-cornered plates. It melts to a clear oil at 167° and effervesces at a higher temperature. Nitrogen determination:

	Calculated for $C_7H_8O_8N_2S$.	Found.
N	14.00	13.72

This acid appears to be stronger than acetic acid, since it was not liberated from its potassium salt by means of an excess of acetic acid. It gives a bulky, white, gelatinous precipitate with alkali and silver nitrate. When warmed with hydrochloric acid, it readily evolves mercaptan and gives uracil-5-carboxylic acid.



Uracil-5-ethylcarboxylate, —Ten grams of the potassium salt of 2-ethylmercapto-5-carbethoxy--6 oxypyrimidine were dissolved, or suspended, in about 75 cc. of strong alcohol, and about 5 cc. of concentrated hydrochloric acid were added. The whole was then boiled with a return condenser for several hours; the alcohol was evaporated and the residue was taken up in about 60 cc. of warm water. The hydrochloric acid was neutralized with ammonia and the solution was then filtered hot. On adding an excess of strong ammonia to the filtrate the ammonium salt of uracil-5-ethylcarboxylate separated as a sponge-like mass of long, slender, colorless needles. This was dissolved in about 50 cc. of water by warming and then a slight excess of acetic acid was added.

On cooling, a granular, crystalline precipitate of the free ester separated. This was found to be very soluble in hot water and moderately so in cold. It was difficultly soluble in alcohol. When crystallized from water it formed flat, sharp-pointed prisms, melting at 236°–237°. Analysis:

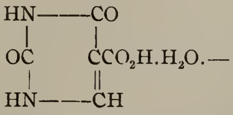
	Calculated for $C_7H_8O_4N_2$.	Found. I.	II.
N	15.21	15.09	15.21

The *ammonium salt* of uracil-5-ethylcarboxylate is characterized by some peculiar properties. When a not too dilute solution of the ester is treated with a little strong ammonia, long, slender needles of the ammonium salt form at once. The vapor from a rod dipped in ammonia and held above the surface of an aqueous solution of the ester will cause crystals to form. When a solution of the salt is boiled, ammonia escapes and, on cooling, nothing separates until more ammonia is added. If the solution is concentrated by heating, the free ester separates. The ammonium salt is insoluble, or difficultly soluble in alcohol. An aqueous solution of the ester was precipitated with ammonia and the precipitate was dried over calcium chloride. The needles thus obtained melted at about 220° to an oil that effervesced. Nitrogen determination (Kjeldahl):

	Calculated for $C_7H_8O_4N_2\ NH_3.H_2O$.	Found.
N	19.13	19.33

When uracil-5-carboxylic ethyl ester is warmed with aqueous hydrochloric acid it is readily saponified and uracil-5-carboxylic acid is obtained.

Uracil-5-carboxylic Acid,



$$\begin{array}{lcl} HN & — & CO \\ | & & | \\ OC & & CCO_2H.H_2O. \\ | & & \| \\ HN & — & CH \end{array}$$

—This acid can be prepared directly from the condensation product of ethoxymethylenemalonic ester and ethylpseudothiourea hydrobromide, or, in other words, from the potassium salt of 2-ethylmercapto-5-carbethoxy-6-oxypyrimidine, without the isolation of the above intermediate products, by simply dissolving the salt in a moderate amount of strong hydrochloric acid and evaporating to dryness on the steam-bath. If the product contains sulphur, the operation is repeated. The residue is then crystallized from water as the acid is practically insoluble in alcohol. It is difficultly soluble in water and separates in the form of colorless, characteristic, minute pyramids with rough faces. Or small prisms form, the faces sometimes alternating with those of a pyramid. The crystals contain $1H_2O$, which is given off on heating above 100°. The acid melts partially, but quite sharply, at 278°, with energetic effervescence. The aqueous solution reddens litmus and it gives no immediate precipitate with lead or copper acetate, or barium chloride. Analysis:

I. 0.5002 gram substance, dried at about 50°, lost 0.0502 gram of water when heated for 1 hour at 122°

II. 0.5486 gram substance lost 0.0561 gram water when heated for 2 hours at 105°–110°.

	Calculated for $C_5H_4O_4N_2.H_2O$.	Found.		
		I.	II.	III.
H_2O	10.34	10.03	10.22	10.02
N	16.09	16.15	16.03	16.26

Nitrogen determination of the anhydrous acid:

	Calculated for $C_5H_4O_4N_2$.	Found.		
		I.	II.	III.
N	17.94	17.88	17.99	17.91

Nitrogen was determined by Kjeldahl's method except in Analysis III. The acid used for Analysis III. (water) and Analysis VI. was obtained by the saponification of uramidomethylenemalonic ester. The other samples were obtained from the potassium salt described above.

Behavior on Heating.—About 0.5 gram of the acid was heated in a test tube, immersed in a sulphuric acid bath, at a temperature a little above its melting point until effervescence ceased. The dark-colored product was boiled with water and animal charcoal and the solution concentrated. On cooling, the characteristic crystals of uracil separated, melting or effervescing at 335°. Analysis (Kjeldahl):

	Calculated for $C_4H_4O_2N_2$.	Found.
N	25.00	24.89

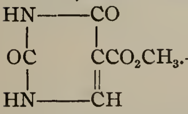
Action of Acids: Formation of Uracil.—The action of 20 per cent sulphuric acid was tried as follows: Fifty-five-hundredths gram of the acid potassium salt of uracil-5-carboxylic acid was sealed in a tube with 5 cc. of sulphuric acid, sp. gr. = 1.15, and heated at 160°–169° for 2 hours. On opening the tube, carbon dioxide escaped and the minute microscopic needles that had separated, after washing with water, were found to melt at 336° without further purification. A nitrogen determination agreed with the calculated for uracil:

	Calculated for $C_4H_4O_2N_2$.	Found.
N	25.00	24.97

The needles weighed 0.25 gram, which amount is 71 per cent of the calculated, or, allowing for solubility, it is practically a theoretical yield.

The Action of Concentrated Hydrochloric Acid.—One gram of uracil-5-carboxylic acid was boiled with about 50 cc. of concentrated hydrochloric acid, using a return condenser, for 18 hours. The acid was then evaporated and the residue was crystallized from water, whereupon over 0.3 gram of uracil separated.

Esterification: Methyl Uracil-5-carboxylate,



—When uracil-5-carboxylic acid is warmed with acids in methyl or ethyl alcohol, it is smoothly esterified. One gram of the anhydrous acid was suspended in 75 cc. of methyl alcohol, to which 5 drops of concentrated sulphuric acid had been added. On boiling for 8 hours, all of the acid went into solution and on evaporation to a small volume a gelatinous mass was formed. This gave a white powder when stirred with cold water. The material thus obtained was readily soluble in hot water and on cooling, short, stout, colorless prisms separated. These sintered at about 225° and decomposed at 233°. Nitrogen determination (Kjeldahl):

	Calculated for $C_6H_6O_4N_2$.	Found. I.	II.
N	16.47	16.62	16.58

When uracil-5-carboxylic acid was warmed with ethyl alcohol and sulphuric acid, the ethyl ester described above was obtained. It was identified by the melting point 236° and by its behavior towards ammonia.

The Acid Potassium Salt, $C_5H_3O_4N_2K.C_5H_4O_4N_2$.—When uracil-5-carboxylic acid and either sodium or potassium hydroxide were mixed, in molecular proportions, the hot aqueous solution, on cooling, deposited an acid salt. For example, 8 grams of the hydrous acid and 2.5 grams of potassium hydroxide were dissolved in about 500 cc. of boiling water. On cooling, 2 grams of slender, needle-like crystals separated. These effervesced at about 270°. Analysis:

	Calculated for $C_{10}H_7O_8N_4K$.	Found. I.	II.	III.
N	16.00	15.89	15.98	.....
K	11.14	.....	.....	10.87

The Monopotassium Salt, $C_5H_3O_4N_2K$.—Three grams of uracil-5-carboxylic acid were dissolved in a solution of 2 grams of potassium hydroxide, 1.9 grams = 2 mols., in about 20 cc. of water; on concentrating on the steam-bath small needles separated. These were dried at about 55°. Nitrogen determinations (Kjeldahl):

	Calculated for $C_5H_2O_4N_2.K_2$.	$C_5H_3O_4N_2K$.	Found. I.	II.
N	12.06	14.43	14.72	14.71

The analyzed material showed no signs of melting at 295°. On dissolving the dried salt in water the solution was found to be neutral to litmus and turmeric. It gave a white, insoluble precipitate with lead acetate and the hot solution gave a crystalline precipitate with barium chloride.

The Barium Salt, $(C_5H_3O_4N_2)_2Ba$.—Barium chloride was added, in excess, to a hot, dilute, neutral solution of the above potassium salt. Stout, microscopic prisms, pointed at both ends, crystallized out. These were almost insoluble in hot water. They were dried at 110°–120° but did not give off water.

	Calculated for $C_{10}H_6O_8N_4Ba$.	Found.
Ba	30.64	28.83

The Silver Salt.—Two grams of the monopotassium salt were dissolved in 100 cc. of water and 1.7 grams of silver nitrate in 50 cc. of water were slowly added, with stirring, in order to prevent a local excess of the nitrate. A white, bulky, gelatinous precipitate separated which did not alter or become granular on warming. The solution was diluted with 100 cc. of water and allowed to settle; the precipitate was washed by decantation and then filtered on cheese cloth. It was dried at 100° for analysis.

One molecular proportion more of silver nitrate was then added to the filtrate. This gave a slight precipitate. On adding 0.5 gram of potassium hydroxide, in a little water, a quantity of white salt was again precipitated, apparently equal in amount to that which was obtained at first. The analytical results did not agree with those calculated for a pure salt. They indicate that the precipitate was a mixture of a mono- and a disilver salt. A sample prepared by taking molecular proportions of acid, sodium hydroxide and silver nitrate gave no better results (Analyses III. and IV.).

	Calculated for $C_5H_3O_4N_2Ag$.	Calculated for $C_5H_2O_4N_2Ag_2$.	Found.			
			I.	II.	III.	IV.
N	10.64	7.56	8.86	8.54	....	....
Ag	41.64	58.37	....	....	49.0	51.5

The following shows that uracil-5-carboxylic acid gives a disilver salt: Eleven grams of the acid, dissolved in water and treated with 2 molecules of sodium hydroxide and 2 molecules of silver nitrate, gave a pure white precipitate which, when dry, weighed 21 grams. The calculated for a mono salt is 16 grams, that for a disilver salt is 23.4 grams.

Dimethyl Derivative.—Ten grams of the disilver salt were suspended in ether and 15 grams of methyl iodide were added.

The mixture was heated in a closed tube at 98°–103° for 1.5 hours. The ether and excess of methyl iodide were evaporated and the residue extracted with alcohol. This gave a gummy extract which, when recrystallized from alcohol, yielded small prisms, melting at 254°–256°, with slight effervescence. The substance dissolved with difficulty in hot alcohol and was moderately soluble in hot water. It had a very bitter taste. A nitrogen determination (Kjeldahl), made after drying at 110°–120°, gave:

	Calculated for $C_7H_8O_4N_2$.	Found.
N	15.21	15.16

A *diethyl derivative* was prepared in a similar manner. It crystallized from alcohol, in which it is moderately soluble when cold, in the form of clusters of blunt prisms, melting at 162°–163°. In both of these reactions of the silver salt the chief product isolated was the free, unaltered acid which was obtained by extracting the residue with water. A nitrogen determination (Kjeldahl), in the case of the material melting at 162°–163°, showed that it was a diethyl derivative:

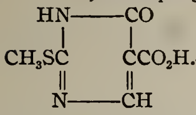
	Calculated for $C_9H_{12}O_4N_2$.	Found.
N	13.20	13.45

Ethoxymethylenemalonic ester and methyl pseudothiourea hydriodide were condensed, using 1 molecular proportion of potassium hydroxide. Under these conditions the free 2-methylmercapto-5-carbethoxy-6-oxypyrimidine did not separate but, instead, a poor yield of a basic hydriodide of the ester was obtained. A nitrogen determination (Kjeldahl) agreed with the calculated for a 2:1 salt:

	Calculated for $(C_8H_{10}O_3N_2S)_2HI$.	Found.
N	10.0	10.1

This salt forms needles from alcohol; when boiled with water, mercaptan was given off. It had no definite melting point.

2-Methylmercapto-5-carboxyl-6-oxypyrimidine,



—This was obtained by warming the above salt with potassium hydroxide and then precipitating with hydrochloric acid. It crystallized from hot water in well developed, colorless prisms, melting, to a clear oil, at 235°. Nitrogen determination (Kjeldahl):

	Calculated for $C_6H_6O_3N_2S$.	Found.
N	15.05	14.71

Our chief experiments were performed with the ethylmercapto derivatives, since they are more insoluble than the methyl compounds.

New Haven, Conn.,
January, 1907.

A POSSIBLE EXPLANATION OF THE INCREASE IN VISCOSITY WHICH RESULTS WHEN THE ALCOHOLS ARE MIXED WITH WATER; AND OF THE NEGATIVE VISCOSITY COEFFICIENTS OF CERTAIN SALTS WHEN DISSOLVED IN WATER.

[SEVENTH COMMUNICATION.]

By Harry C. Jones and W. R. Veazey.

It is well known that when methyl or ethyl alcohol is mixed with water the viscosity of the mixture is much greater than that of either pure liquid. The following seems to us to be a possible explanation of this phenomenon:

It was shown some time ago by Jones and Murray[1] that when 2 associated liquids, such as formic acid and water, or acetic acid and water and, probably, such as alcohol and water, are mixed, each diminishes the association of the other. The result would be that in such a mixture there would be present a *larger number of smaller molecules* than if the two liquids simply mixed without affecting each other's association.

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[1] This Journal, 30, 205 (1903).

This diminution in the association of the liquid molecules, increasing their number and diminishing their size, would increase the viscosity by increasing the total frictional surfaces of the molecules that would come in contact with one another—the smaller the molecules the larger the total surfaces of the molecules for a given mass of the liquid.

The above point can be illustrated by means of small shot and large shot. For a given mass, the smaller shot moving over one another would produce greater friction than the larger shot, due to the larger frictional surfaces that would come in contact. The same applies to the molecules of the mixed solvents.

The comparatively small association of the molecules of the mixed solvents, explains another phenomenon which has manifested itself in a number of the investigations[1] recently carried out in this laboratory. In those mixtures of solvents where the *viscosity is a maximum, the conductivity curve of many dissolved electrolytes shows a minimum.* As the conductivity curves, for the solutions of different concentrations of a given salt in different mixtures of 2 solvents, *approach the minimum, they approach one another.* This means that the molecular conductivities do not increase rapidly in these particular mixtures of the 2 solvents, with change in the dilution of the solution. This is exactly what would be expected if the molecules of the solvents in the mixture were only comparatively little associated. They would then have comparatively little dissociating power, and the conductivity in such a mixture of solvents would increase only slowly with increase in the dilution of the solution. The curves for molecular conductivity would, therefore, approach one another, as they approach the minimum.

It was observed in the course of our work that solutions of potassium sulphocyanate in water are *less viscous than pure*

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[1] Jones and Lindsay: THIS JOURNAL, **28**, 329 (1902). Jones and Carroll: *Ibid.*, **32**, 521 (1904). Jones and Bingham: *Ibid.*, **34**, 481 (1905). Jones and McMaster: *Ibid.*, **36**, 325 (1906).

water. On looking up the literature that bears upon this problem, and especially the work of Wagner,[1] we find that a number of salts show this negative viscosity coefficient. They are potassium chloride, potassium nitrate, rubidium chloride and caesium chloride. Thallous nitrate also, apparently, shows the same phenomenon.

The explanation of this *negative viscosity coefficient* is comparatively simple, in the light of what has already been said in reference to viscosity.

The salts with the negative viscosity coefficient are, then, certain salts of potassium, rubidium and caesium. The case of thallous thallium will be considered a little later. If the *ions of the salt were very large*, relative to the molecules of the solvent, then the effect of the dissolved substance on the viscosity of the solvent would be to diminish it. This will be seen at once, if we think of a number of larger spheres mixed with a much larger number of smaller spheres. The frictional surfaces would be diminished and, consequently, the friction, when these spheres move over one another.

The question is whether there is any reason to suppose that the ions of potassium, rubidium and caesium are large. If we turn to the curve of atomic volumes[2] we find the answer. As is well known, potassium, rubidium and caesium occupy the maxima of the atomic volume curve, and these 3 elements have *much larger atomic volumes* than any other known elements.

The *qualitative* agreement of fact and theory are thus in accord, with the exception of the thallous salt. Since, however, we do not know at present the atomic volume of thallous thallium, this case will have to be left out of the discussion.

If we wish to test the above suggestion *quantitatively*, we have the means of doing so. Potassium has a much larger atomic volume (about 47) than any other element except rubidium and caesium. The atomic volume of rubidium is about 57, while the atomic volume of caesium is about 74. If we compare the viscosities of the same salt of these 3 elements, say the chlorides, we should expect to find, in terms of our hypothesis, that the viscosity coefficient would be less for rubidium chloride than for potassium chloride, and less for caesium chloride than for rubidium chloride.

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[1] Z. physik. Chem., 5, 31 (1890).

[2] Lothar Meyer: Die Moderne Theorien der Chemie; Holleman: Inorganic Chemistry; Jones: Elements of Physical Chemistry.

From the work of Wagner we can make the above comparison. The time of flow of pure water through the viscometer is taken as the unit of value for η. The values of η for normal solutions of potassium chloride, rubidium chloride and caesium chloride are:

	η.
Potassium chloride	0.9872
Rubidium "	0.9846
Caesium "	0.9775

It is worth noting that the difference between the values of η for caesium chloride and rubidium chloride is much greater than the difference between rubidium chloride and potassium chloride. This is in keeping with the relative atomic volumes of the 3 elements. The difference between the atomic volume of rubidium and caesium is much greater than the difference between the atomic volume of rubidium and potassium.

The question now arises whether, *e. g.*, all potassium salts show the negative viscosity coefficient. The answer is that they do not. The reason for this is obvious when we consider that the effect of a salt on the viscosity of a solvent is an additive function of both of the ions present in the solution. The anion, so far as we know, always tends to increase the viscosity of water, while certain cations, as those above considered, diminish the viscosity of water. The action of the salt, as a whole, upon the viscosity of water, is the algebraic sum of these effects, which may be either positive or negative.

Wagner[1] studied 6 salts of potassium in this connection, and found values of η less than unity only in the case of the chloride and nitrate. In the other 4 cases the action of the anion more than overcame the effect of the cation, and η was always greater than unity. *The chloride gave a negative value for η.* This would be expected, since *chlorine has itself a large atomic volume*; indeed, larger than that of any other elementary anion except bromine. This would, then, probably act in the same way as the potassium cation, giving a negative coefficient; or, if the coefficient due to chloride were positive, it would have a very small value.

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[1] Z. physik. Chem., **5**, 36, 37 (1890).

For the same reason potassium nitrate shows a large negative viscosity coefficient.

If we extend the above conception to other cations with large atomic volumes, but with much smaller atomic volumes than the 3 alkalies, we shall find that it holds satisfactorily. Taking calcium, strontium and barium, which, of all cations, have the next larger atomic volumes, and comparing their chlorides with respect to the values of η, we have, for normal solutions:

	η.
Calcium chloride	1.1563
Strontium chloride	1.1411
Barium chloride	1.1228

These values are all positive, as we should expect them to be, but their order is exactly *the reverse of the atomic volumes*, just as would be expected.

Chlorides with cations of still smaller atomic volumes have values of η much larger than the above. This will be seen from the following table, where all the values of η refer to normal solutions. In the same table are given the approximate atomic volumes of the cations of the several chlorides:

	At. vol.	η.
Magnesium chloride	14	1.2015
Cupric "	8	1.2050
Manganous "	7	1.2089
Nickel "	7	1.2055
Cobalt "	7	1.2041

It is obvious that for the atomic volumes of the same order of magnitude, the values of η are of the same order of magnitude; and, in general, the larger the atomic volume the smaller the value of η, just as we should anticipate in terms of our hypothesis.

The small values of η for zinc, cadmium and mercury are probably due to the fact that the salts of these metals are only slightly dissociated.

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STUDIES IN CATALYSIS: THE REARRANGEMENT OF ACETYLHALOGENAMINOBENZENE DERIVATIVES INTO HALOGEN ACETANILIDE DERIVATIVES.

BY S. F. ACREE AND J. M. JOHNSON.

[The writers are indebted to the Carnegie Institution of Washington for aid in this work.]

Acetylchloraminobenzene[1] rearranges in the presence of hydrochloric acid into parachloracetanilide, but is stable under alkaline solutions. Blanksma[2] found that the velocity of the rearrangement increases as the square of the concentration of the acid increases, and that the reaction is one of the first order, or, apparently, monomolecular.

We have now found that the catalytic action of the acid is not due merely to the presence of the hydrogen ions, but that the acid unites with the acetylhalogenaminobenzene and forms another compound which rearranges into the halogen acetanilide,

$$(1)\ CH_3CONClC_6H_5 + HCl \rightleftarrows CH_3CONHCl_2C_6H_5 \rightleftarrows CH_3CONHC_6H_4Cl + HCl.$$

Acetylchloraminobenzene and hydrobromic acid give parabromacetanilide and the same product is obtained from acetylbromaminobenzene and hydrochloric acid. This is due to the fact that the bromine migrates much more rapidly than the chlorine to the benzene ring. Similarly, chlorine

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[1] Slosson: Ber. d. chem. Ges., **28**, 3265. Armstrong: J. Chem. Soc., **77**, 1047. Chattaway and Orton: *Ibid.*, **75**, 1046; **77**, 134; **79**, 274; Ber. d. chem. Ges., **32**, 3573.

[2] Rec. Trav. Chim., **21**, 366; **22**, 290.

$$(2)\quad \begin{array}{l} \mathrm{CH_3CONClC_6H_5 + HBr} \searrow \\ \mathrm{CH_3CONBrC_6H_5 + HCl} \nearrow \end{array} \mathrm{CH_3CONHClBrC_6H_5} \rightarrow \mathrm{CH_3CONHC_6H_4Br + HCl.}$$

and bromine cause the change of acetylchloraminobenzene in a few seconds, in ligroin solution, into parachloracetanilide and parabromacetanilide, respectively. Quantitative measurements have shown the velocity constant for the change of acetylchloraminobenzene by hydrobromic acid to be about 1000 times as great as that for hydrochloric acid in the same concentration. Since solutions of sulphuric, acetic, hydrochloric and hydrobromic acids, having the same concentration of hydrogen ions, give different velocity constants, it is evident that the catalysis is not dependent directly upon the concentration of the hydrogen ions. The reaction between the hydrobromic acid and acetylchloraminobenzene is of the second order, whereas that produced by hydrochloric acid is of the first order, as demanded by equation (2).

The reaction is not dependent upon the rearrangement of an intermediate cathion formed from the weak base acetylhalogenaminobenzene and the hydrogen ions, as is probably the case in the hydrolysis of such weak bases as esters, amides, amidines and oximes. If such were the reaction, we should have, from Walker's equation,

$$(3)\qquad \mathrm{CH_3CONClC_6H_5} + \overset{+}{\mathrm{H}} \rightleftarrows \mathrm{CH_3CO}\overset{+}{\mathrm{N}}\mathrm{HClC_6H_5};$$

or

$$(4)\qquad C_{\mathrm{base}} \times C_{\mathrm{H}} = KC_{\mathrm{salt}}.$$

The velocity of transformation of the substance would then be

$$(5)\qquad \frac{dx}{dt} = K_{\mathrm{trans}}\, C_{\mathrm{salt}} = \frac{K_{\mathrm{trans}}\, C_{\mathrm{base}} \times C_{\mathrm{H}}}{K},$$

or the velocity of rearrangement would be proportional to the concentration of the hydrogen ions, as we actually find in the formation and saponification of esters, and the hydrolysis of acetamide.

But if the rearrangement is that of an intermediate undissociated salt, as was shown above, since the salt is greatly hydrolyzed and the small amount present is nearly completely dissociated, we have from the mass law:

$$(6) \quad CH_3CONClC_6H_5 + \overset{+}{H} + \overset{-}{Cl} \rightleftarrows CH_3CONHCl_2C_6H_5,$$

or

$$(7) \quad C_{\text{base}} \times C_H \times C_{Cl} = KC_{\text{salt}} = C_{\text{base}} \times C_H^2 = C_{\text{base}} \times C_{Cl}^2.$$

The velocity of transformation of the substance would then be

$$(8) \qquad \frac{dx}{dt} = K_{\text{trans}}\, C_{\text{salt}} = \frac{K_{\text{trans}}}{K}\, C_{\text{base}} \times C_H^2,$$

which is what is actually found experimentally. A further fact in support of this view is that the velocity of rearrangement becomes slower in those acetic acid solutions containing a greater percentage of water.

We have here a case, then, in which the velocity of a reaction is not proportional to the concentration of the catalyzing hydrogen ions, but to the square of that concentration. This fact at once leads to the conclusion that some reversible reaction may yet be found in which the equilibrium is changed by a change in the concentration of the catalyzer. The velocity of the reaction in one direction may be proportional to the m power of the concentration of the catalytic agent, whereas the velocity of the reverse reaction may be proportional to the n power of the concentration of the catalyzer, or

$$(9) \qquad \frac{KC_{\text{sub}}}{K'C_{\text{sub}'}} = (C_{\text{cat}})^{\frac{m}{n}}.$$

Such a case seems to have been discovered recently by Baur and Voerman,[1] who showed that chromium nitride is a very energetic catalyzer of ammonia, in effecting its own formation from chromium and ammonia, but has no great influence on the reverse reaction, or the formation of ammonia from hydrogen and nitrogen:

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[1] Z. physik. Chem., 52, 467.

$$Cr + NH_3 \rightleftarrows CrN + 3H.$$

The above theory of intermediate compounds in catalytic reactions is being investigated in several directions in this laboratory. We shall continue the study of the rearrangement of acylhalogenaminobenzene derivatives and other similar rearrangements.

JOHNS HOPKINS UNIVERSITY.

OBITUARY.

NICOLAI ALEXÁNDROWITSCH MENSCHUTKIN.

In the course of a few weeks Russia has lost her three most eminent chemists, Beilstein, Mendeléeff and Menschutkin.

Professor Menschutkin was born in St. Petersburg, October 12, 1842, and died in the same city February 5, 1907. He received the doctor degree from the University of St. Petersburg in 1866, and became professor of chemistry in the same institution in 1876. In 1902 he retired with the title of Professor Emeritus, but during the same year was appointed professor in the St. Petersburg Polytechnium. From 1868 to 1900 Menschutkin was editor of the "Journal of the Russian Physical-Chemical Society," and he wrote several text-books on analytical, organic and theoretical chemistry, and also a biographical dictionary of the professors of the University of St. Petersburg during the years 1869–94.

Menschutkin's fame as a chemist is based on his study of the velocity of certain organic reactions, especially those leading to the formation of esters and of ammonium derivatives. Besides investigating the influence of temperature, dilution, etc., on the velocity and conditions of equilibrium, he gave special attention to discovering the effect on ester formation, of difference in structure both of acids and alcohols, and was able to show how sharply and clearly the values measured by the physical chemist are correlated with the structural formulae assigned by the organic worker. Menschutkin was Vice-president of the Russian Physical-Chemical Society and a Foreign Member of the Chemical Society (London).

HENRI MOISSAN.

Professor Henri Moissan was born in Paris, September 28, 1852, and died in the same city, after an operation for appendicitis, February 20, 1907. Moissan spent his whole life in Paris; his doctorate was from the University of that city, and at the time of his death he was Professor of Chemistry at the Sorbonne and Director of the Laboratory of Mineralogical Chemistry. Moissan's fame as a chemist does not rest only on his great discoveries—the isolation of fluorine, the artificial production of the diamond and the invention and utilization of the electric furnace—his wonderful technique, his thoroughness, and the beauty, simplicity and modesty of the language in which his results were communicated to the world, had no small share in carrying instant conviction to any reader that the problem under consideration had been dealt with as fully and completely as contemporary skill and appliances permitted. His later work has been concerned largely with the preparation of binary compounds of the metals and non-metals; although less dramatic and, therefore, perhaps, less widely known than some of his earlier researches, such as that on artificial diamonds, it demanded as great, if not greater, skill and resource. It has led to the preparation by him, in the electric furnace, of large numbers of carbides, nitrides, silicides, borides, phosphides, etc.

Some of these substances have acquired considerable technical importance; all of them are of interest to the pure Chemist, but they appeal to a still wider circle. When their mode of formation and properties shall have become familiar to the Geologist, they can hardly fail to modify profoundly many of the present theories regarding the age and past history of the earth.

In contrast to his experiments with the electric furnace, his investigations on the possible existence of ammonium, NH_4, and other similar substances may be mentioned. Although he failed to obtain this complex, the researches demonstrated that his skill and fertility of resource, and the beauty and simplicity of the appliances which he designed were as great when working at the lowest, as at the highest attainable temperatures.

Moissan's books shared the same purity of diction and clarity of style which marked his papers. Besides those dealing with his own experiments, he edited the "Traité de Chimie Minérale," in 5 large volumes.

Moissan was the recipient of many marks of distinction from his fellow-chemists. He was a member of the Institute of France, Foreign Member of the London Chemical Society and Honorary Member of the American and German

Chemical Societies. He was the French member of the "International Committee on Atomic Weights," and at the end of last year was awarded the Nobel Prize.

HENDRIK WILLEM BAKHUIS-ROOZEBOOM.

Professor Bakhuis-Roozeboom was born at Alkmaar, North Holland, October 24, 1854, and died rather suddenly at Amsterdam, February 8, 1907. Roozeboom spent the whole of his active life at Leiden and Amsterdam. He was appointed Assistant in Chemistry in the former University in 1878, received the doctor degree from it in 1884, and was promoted to be "Lector" in 1890. Since 1896 he has been Professor of Inorganic and Physical Chemistry at the University of Amsterdam. Roozeboom is best known for his extensive researches into the nature of mixed crystals, of double salts and of racemic compounds, and for his work on the application of the phase rule to the results which he obtained from these investigations. He made numerous studies of heterogeneous equilibria from the phase rule standpoint, and published a volume on the subject in 1901. Roozeboom was an honorary member of the American Chemical Society.

REPORT.

Glyoxal.

The properties of the compound known as glyoxal are certainly not such as would be expected of a substance with the formula OCHCHO. Some text-books try to evade this difficulty by describing the body as a "hydrate" but, to say the least, this is unsatisfactory. C. Harries and Paul Temme[1] have made recently an important contribution to our knowledge of this interesting compound. Glyoxal exists in the following 4 forms: (1) Monomolecular glyoxal, OCHCHO, which is unstable and is described more fully below. (2) A trimolecular modification, $(C_2H_2O_2)_3$, which may possibly have the formula OCHCH(OH)COCH(OH)COCHO. It is a colorless, pulverulent solid, readily soluble in water and forms no characteristic derivatives, *i. e.*, reagents give with it only derivatives of 1. (3) Paraglyoxal, $(C_2H_2O_2)_x$, a white powder, insoluble in water. (4) The ordinary form of glyoxal, termed polyglyoxal, $(C_2H_2O_2)_n$. This was discovered 50 years ago by Debus, and is the substance described in text-books and in catalogues of chemicals. Compound No. 2 reduces Fehling's solution, but Nos. 3 and 4 do not.

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[1] Ber. d. chem. Ges., 40, 165 (1907).

Monomolecular glyoxal is prepared by distilling a mixture of technical "glyoxal" (4) with phosphorus pentoxide, and condensing the distillate by means of solid carbon dioxide and ether. Care must be taken to avoid the presence of moisture in the apparatus. The compound crystallizes in yellow prisms or spangles, becomes opaque at 10°, melts at 15° and boils at 51° (776 mm.), or 50° (742 mm.). The vapor is intensely emerald-green and condenses to a liquid which is at first green; as this is cooled it becomes yellow and, at very low temperatures, colorless. The vapor has an odor like that of formic aldehyde, but as inhalation continues the smell becomes sweet and not disagreeable. It burns with a violet flame and forms with air a mixture which explodes violently on the application of a flame. Glyoxal changes spontaneously into paraglyoxal (3) in a few hours. Its vapor density and refractive power agree with the simple formula. Its reaction with water is very interesting. The addition of a small quantity of water to glyoxal causes immediate polymerization to paraglyoxal (3), whereas, if glyoxal be added to a large quantity of water, it dissolves readily with a hissing noise and the solution, which becomes decidedly acid, contains monomolecular glyoxal, as is shown by cryoscopic measurements. If this solution is boiled, the glyoxal volatilizes with the steam. It reduces ammoniacal silver solution, but not Fehling's solution, in this latter respect resembling the poly- and para-modifications. It is chiefly on this fact that the formula for trimolecular glyoxal is based.

Trimolecular glyoxal is readily prepared by the action of water on cinnamic aldehyde ozonide.[1] The oily product, consisting of benzoic acid and, apparently, of benzoic aldehyde, is removed, and the aqueous solution concentrated at 30°–40°, *in vacuo*. If the temperature is allowed to rise above 40°, the substance finally isolated resembles commercial glyoxal (4) more or less closely, and has, to a varying degree, the power of reducing Fehling's solution.

Attention may be called to the fact that in being strongly colored, monomolecular glyoxal resembles the α-diketones, such as diacetyl. Moreover, of the compounds containing only carbon, hydrogen and oxygen, glyoxal is probably the simplest one to possess a color. It is of interest to remember, in this connection, that oxalic acid shows not the slightest sign of color, although it also contains the grouping OCCO,
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[1] Cf. This Journal, 35, 463 (1906).

but, of course, with 2 hydroxyls instead of 2 hydrogen atoms. The study of these 2 substances by Baly's method[1] could hardly fail to yield results of considerable interest.

J. BISHOP TINGLE.

REVIEWS.

THE HISTORICAL DEVELOPMENT OF CHEMISTRY. By WILHELM OSTWALD. [Reprinted from the School of Mines Quarterly, Vol. XXVII, Nos. 2–4]. New York. pp. 84.

As stated by the author, this pamphlet is made up of six lectures delivered in the Department of Chemistry of Columbia University in January and February, 1906. The lectures were reported stenographically. Ostwald is always interesting and always thoughtful, perhaps interesting because thoughtful. He is, as he himself says, a philosopher. He is looking for the hidden causes of phenomena, and trying to distinguish the essential from the non-essential. He has a mortal terror of hypotheses. He clearly recognizes the danger connected with their use, but apparently does not recognize their value, or at all events he minimizes it.

In discussing the difference between mixtures, solutions and chemical individuals he says: "Mixtures are therefore substances which can be identified as *heterogeneous* by physical means. Solutions are substances which are *homogeneous*. But now what is the difference between a solution and a chemical individual?" * * * * "To describe this difference in scientific terms I shall have to go back to a most important work of Josiah Willard Gibbs, late professor of mathematical physics at Yale University, and I do not hesitate a moment to speak of him as by far the greatest scientist America has as yet produced." He then gives a brief exposition of the phase rule and proceeds thus: "When, therefore, we wish to know if a homogeneous thing is a solution, a substance, or a chemical individual, we have only to change it to another phase; if in this changing into another phase the change is connected with no change in the remaining portion, then it is a chemical individual. Otherwise it is a solution."

His definition of an element is this: "*An element is a substance or chemical individual which never becomes a solution or mixture.*"

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[1] THIS JOURNAL, 36, 213 (1906).

The discussion of the atomic hypothesis and the law of combining weights furnishes a good illustration of the author's effort to eliminate the hypothetical. That we *can* deal with the laws of definite and multiple proportions and with combining weights without mentioning or even assuming the existence of atoms is well known, but whether anything is gained by doing so is questionable, to say the least. The general opinion among thinking chemists is that the atomic hypothesis does more good than harm.

In treating of the molecular hypothesis the author admits that by its aid "the whole system of organic chemistry can be made much more simple and much more logically related than otherwise." He goes on to say: "Then after this served as an introduction, the molecular hypothesis in chemistry went on rather quickly and emphatically. You will find certain definitions in every text-book—I have not been able to trace the first inventor, but it would be interesting to do so—that atoms are the smallest possible parts of matter which cannot be divided any more, or which, by division, would yield other kinds of matter, and molecules are the smallest particles existing in gases or capable of existing in gases. Now it is the queerest thing that no body ever tried to carry out any experiments to show the truth or to show the scientific meaning of these definitions. Nobody tried to find the smallest particle of a gas and determine its quantity."

The writer of this notice, in his blindness, has hitherto supposed that both the atomic hypothesis and the molecular hypothesis are in harmony with a very large number of facts that have been established experimentally. If this be true, then both hypotheses can be said to have a broad experimental basis. If it were possible to isolate an atom and a molecule and to show by worldly means that they are what we assume them to be, we should all rejoice, but the prospects are not alluring. Meanwhile, must we wait until evidence of this kind shall have been presented?

Of course, organic chemistry comes in for a fling. The author thinks that it is *possible* to deal with all the facts of this branch of chemistry without the assumption of atoms and linkage of atoms. He adds: "*I* think it is possible, but it would be an enormous task, and would take a young man who has still his entire life potential to exert, for this will be a very large and difficult piece of work." I. R.

TOXICOLOGY, THE NATURE, EFFECTS AND DETECTION OF POISONS WITH THE DIAGNOSIS AND TREATMENT OF POISONING. By CASSIUS M. RILEY, M.D., Professor of Chemistry and Toxicology in Barnes University, and Dean of the Barnes College of Pharmacy, etc. Third Edition Revised and Enlarged. Philadelphia: P. Blakiston's Son & Co. 1906. pp. 215. Price, $1.50 net.

The author states that he has sought to present to the busy practitioner a convenient work of reference which contains in concise form the present-day knowledge on this subject. The book differs in no essential way from many others which have appeared. Such statements as the following (p. 8) could have been omitted with profit: "——the more unstable alkaloids and poisons are oxidized in their passage through the lungs." And again on the same page, "Phagocytosis is still disputed by some investigators, but the weight of opinion seems to favor the theory . . . ." etc., etc. Each poison is considered under the following heads: Properties of the Substance, Symptoms, Diagnosis, Fatal Dose, Fatal Period, Treatment, Post Mortem Appearances, Detection. All elaborate chemical methods are omitted. Thus, even Marsh's test for arsenic is not given. The style is clear and concise and the book answers the purpose of the author very well, that is, it will prove a handy book for physicians. A. S. L.

AUSFÜHRLICHES LEHRBUCH DER PHARMAZEUTISCHEN CHEMIE. Bearbeitet von DR. ERNST SCHMIDT, Geh. Regierungsrath, O. Professor der pharmazeutischen Chemie and Direktor des pharmazeutisch-chemischen Instituts der Universität Marburg. Erster Band. Anorganische Chemie. Erste Abtheilung. Metalloide. Fünfte vermehrte Auflage, mit zahlreichen Abbildungen und einer farbigen Spektraltafel. Braunschweig: Fr. Vieweg u. Sohn. 1906. pp. 523. Price, M. 10.

This first instalment of Vol. I. of Professor Schmidt's well-known handbook deals with general chemistry, 114 pp., and with the non-metals, 404 pp.

In the chapter on general chemistry the author makes brief mention and explanation of electrolytic dissociation, mass action and other modern views. The remainder of the volume is purely descriptive. All laboratory and technical methods of preparing elements and compounds are very fully described; for example, 2 pages are given to the preparation of basic bismuth nitrate and to tests of its purity. There are detailed instructions in analytical methods; for example, of 38 pages given to the discussion of water, 23 are filled with details of water analysis; of 12 pages given to phosphorus, 5 describe its detection. We see, then, that this is not a text-book of inorganic chemistry in the ordinary sense, but a combination of one with analytical and preparative treatises.

The system of quarantining chemical theory in an initial chapter—apparently lest the purely descriptive matter should "catch" some germ of theory—is a method very common in German text-books of the period preceding Ostwald, and survives in later editions of such books. Generally, the system is open to severe criticism, but in the present case there is much to be said in favor of it. No one would use Professor Schmidt's book who had not previously studied chemistry with the help of a smaller work, and the practical use of this volume is as a reference and handbook for pharmacists; for this purpose the arrangement is excellent.

The revision seems thorough; but few omissions are noticeable; no mention is made of the solidification of oxygen, nor of the hydrides NaH and KH, though the alloys of these metals with hydrogen, K_4H_2 and Na_4H_2, approximately, are referred to.

In brief, the first instalment of Professor Schmidt's book indicates that the work, as a whole, will retain its high position as a handbook almost indispensable to pharmacists.

E. R.

THE CHEMISTRY AND PHYSICS OF DYEING. By W. P. DREAPER, F.I.C., F.C.S. Illustrated by Curves and Numerous Tabulated Results. Philadelphia: P. Blakiston's Sons & Co. 1906. Price, $3.00 net.

Although many investigators have published independent articles in regard to the purely scientific relations existing between textile fibers and coloring matters, the above work is the first, in the English language at least, which brings together in one volume a general record of the important work that has been done along this line.

The modern textile colorist is so absorbed with the commercial success of his work, that he overlooks the fact that a more thorough knowledge of the physical and chemical relations existing between fiber and coloring matter would, ultimately, lead to the improvement of the processes he is using, as well as to the introduction of great economies. Many of the more progressive textile colorists undoubtedly realize the desirability of such a knowledge, but the demands upon their time are such that it is impossible for them to go through all the journals and extract from this and that one the facts which have been discovered and the theories which have been formulated by the many investigators. To such, this volume will prove of great value, for the author has succeeded in bringing together the essence of the work of many workers, and with the interjection of certain views of his own, has presented an interesting and valuable résumé of the work that has been done by the scientist toward the elucidation of the exact nature of the process of textile coloring.

The historical introduction goes back to a period 1500 B. C., when wool dyed with the celebrated Tyrian Purple, sold for a price corresponding to $150 per pound, and includes a bibliography of the early publications in regard to dyeing. In this connection it might be noted that the extensive works of Edward Bancroft, M.D., one of the pioneer investigators, which were published between 1769 and 1814 were overlooked, although reference is made later in the book to Bancroft's classification of dyestuffs into substantive and adjective coloring matters, which for many years was about the only accepted classification.

The chapter on the properties of the fibers and their reactions enumerates the important facts which have been discovered concerning the chemical nature of the textile fibers and their action in contact with reagents. The author's statement to the effect that the complex chemical nature of the textile fibers has rendered the knowledge in regard to them very limited and unsatisfactory is, unfortunately, too true, but as the study of colloid substances is continued and new facts are discovered in regard to their nature, it is hoped that much can be done toward clearing up many relations existing between fibers and coloring matters which are but little understood at the present time. The author has certainly taken the proper view of the matter, for it is evident that he thoroughly believes that the keynote to the interpretation of the facts already discovered, and the hopes of future development, depend largely upon our present knowledge of solution and the properties of colloids and the advancement that may be made through their study.

The 3 long chapters which treat, in the main, upon solution and colloids, are well worth the careful study of the textile chemist and colorist, for one cannot help being introduced to entirely new lines of thought and reasoning when they are taught to apply the principles of the modern science of physical chemistry to their study of the phenomena of textile coloring.

Whether or not the dyeing process is, in the majority of cases, of a physical or a chemical nature, is still an open question, but during recent years chemists have come more and more to believe that chemical action is involved in the application of many dyestuffs, particularly the two classes known as the acid and basic coloring matters. In the 2 chapters entitled, "Evidence of Chemical Action in Dyeing," the author presents, in a systematical manner, all the evidence he has been able to collect from the journals and the writings of investigators, as far back as Dufay in 1737, but, as he says in the closing paragraph, "Until the time comes when we are able to explain the actions which take place when colloids react in the presence of solvents and definitely assign to these phenomena their true nature, it will be difficult to establish a strictly chemical basis for the reactions which take place in dyeing."

Another chapter deals with the influence of light during dyeing operations and upon dyed fabrics, subjects in regard to which but little exact information is obtainable, but the author goes into considerable detail with the material at hand.

The closing chapter of the book, entitled "Methods of Research," though short, is very expressive of the general spirit of the whole book, namely, a plea for more thorough, exact and extensive investigation of the fundamental facts and theories of the various textile coloring operations. The author should be given credit for having been willing and able to break away from the purely commercial aspect of the subject, and for having presented a work which must necessarily set many readers to thinking along new channels and prove an element in the uplifting of textile coloring as a more exact science.

L. A. OLNEY.

ESSENTIALS OF CRYSTALLOGRAPHY. By EDWARD HENRY KRAUS, Ph.D., Junior Professor of Mineralogy, University of Michigan. 8vo, pp. xl + 162 and 427 figures. Ann Arbor, Mich.: Geo. Wahr. 1906. Price, $1.60.

This little book, prepared by Professor Kraus, will doubtless prove serviceable to instructors in crystallography, because of its many illustrations and tables of crystal forms. It may likewise prove serviceable to chemists familiar with the older forms of crystallographic nomenclature, since these are here brought into association with the new terms based on 32 classes. The free use of varied standard text-books recognized in the preface is evident throughout the book. Without wishing to criticize severely, the reviewer questions the advisability of retaining the old method of discussing hemihedrism and hemimorphism by the assumption of the suppression of given faces. Each suppression is contrary to the methods of formation of the so-called partial forms, and the advantages arising therefrom are not equal to the misconceptions which the student almost always acquires.

E. B. M.

NOTES ON MILITARY EXPLOSIVES. By ERASMUS M. WEAVER, Major, Artillery Corps, U. S. Army; General Staff Detail. Late Instructor in charge of the Department of Artillery Chemistry and Explosives, Artillery School, Fort Monroe, Va., and Artillery Inspector Atlantic Division. First Edition. New York: John Wiley & Sons. 1906. pp. 311. Price, $3.00 net.

The author says: "These notes were collected with a view to lecturing on the subject of Modern Military Explosives to the student officers at the Artillery School, Fort Monroe, Va. It was desired to give the officers a general knowledge of the modern explosives, including the composition and manufacture of the important military explosives; the general chemical and physical principles involved in explosive phenomena; the principles governing the storage, handling and uses of explosives in demolitions and disruptive work."

The book seems, on the whole, well adapted to the purpose. The author, from a military point of view, divides explosives into 3 classes: Progressive or propelling; detonating or disruptive; and exploders. The first class includes charcoal powders and nitrocellulose powders; the second includes guncotton, nitroglycerin, dynamite, explosive gelatin, and derivatives of picric acid; the third treats of fulminates.

The chapters on the storage and handling of explosives and their use for demolitions are excellent, as would be expected from an author who knows the subject both practically and theoretically, and has also had the teachers' experience.

The least satisfactory part of the volume is the introductory chapter on the principles of chemistry, in 47 pages. This chapter is included because "some of the officers have little or no knowledge of chemistry." This would, doubtless, be a bar to an intelligent study of explosives, but that the deficiency could be made good by studying the extremely condensed material given here, even with laboratory work, seems doubtful. E. R.

BEET-SUGAR MANUFACTURE. By H. CLASSEN, Ph.D., translated from the Second German Edition by Wm. T. Hall and Geo. Wm. Rolfe, Instructors in the Massachusetts Institute of Technology. New York: John Wiley & Sons; London: Chapman & Hall, Ltd. 1906. pp. xiv + 280. Price, $3.00 net.

This book gives a condensed review of the principal processes involved in the manufacture of beet sugar. It brings the technique of the processes up to the year 1903. The rapid growth of the beet sugar industry in this country justifies the publication of elementary works of the character of the present one. The translators have done the original into good English, and placed the work at the service of the non-

German reading expert. There is nothing new or novel in the contents of the book. It is interesting to note that the author considers lime and carbon dioxide as the best and cheapest agents in the purification of the diffusion juice. He states that the use of sulphurous acid, aluminum sulphate and the electric current has not been proved profitable or advisable. It is, doubtless, true that the same principle holds with cane juice, and the use of such injurious substances as sulphurous acid will probably soon cease, especially when the resulting molasses is intended for human food. A most interesting chapter, from a technical point of view, is that relating to the treatment of sludge or scums. This matter is presented in admirable form. The chapter on sugar is given in detail and will be found especially valuable to beginners. A useful chapter is also that devoted to molasses and its utilization, particularly its consumption as a cattle food. The final chapter, on the utilization of the waste products, is also interesting. The appendix contains formulae, tables of data, etc.

The work will be found useful to those engaged in the cane sugar industry, as well as to those who manufacture sugar from the beet.

H. W. WILEY.

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AMERICAN

CHEMICAL JOURNAL

THE OSMOTIC PRESSURE OF CANE SUGAR SOLUTIONS IN THE VICINITY OF THE FREEZING POINT OF WATER.[1]

By H. N. Morse, J. C. W. Frazer and W. W. Holland.

To prepare for the measurement of osmotic pressure at low temperatures, an ice box of galvanized iron was suspended in each end of the bath which was described in a former paper.[2] The boxes consisted of superimposed and readily separated sections. The lowest of these extended from near the bottom of the tank to a short distance above the surface of the water, and they were held in their positions by means of lugs, riveted to the sides, which rested upon the top of the tank. They were provided with perforated bottoms. The sides were also perforated below the water line in order to insure a free circulation of water about the ice. The higher sections of the boxes were without bottoms, and served merely as lateral retainers for the ice. Each box extended upward in the air space to a height somewhat above the tops of the manometers, and each contained, when filled, about 75 kilograms of ice. Above the space between the boxes, and resting on their adjacent rims, was a galvanized iron tray, as wide as the tank, which was likewise filled with ice. Still further provision for cooling the air space above the water was made by placing a narrow ice box in the rear of the bath behind the manometers.

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[1] The work upon osmotic pressure which is in progress in this laboratory is aided by grants from the Carnegie Institution. The papers upon this subject which have preceded the present one will be found in This Journal: **26**, 80; **28**, 1; **29**, 173; **32**, 93; **34**, 1; **36**, 1, 39; and **37**, 324.

[2] This Journal, **36**, 1.

By means of the pumps, which were described in a former paper,[1] the water in the bath was kept in constant motion, and the air above it was made to circulate through the pipes lying in the water. To maintain a constant level, the surplus water, resulting from the melting of the ice, was continuously removed by means of a siphon with limbs of equal length and upturned ends. The horizontal portion of the siphon passed through one of the end walls of the bath, leaving one of the curved ends of the tube submerged in the water in the tank, and the other suspended over a waste pipe on the outside of the bath.

The extreme variations in the temperature of the water during the entire work were between 0°.12 and 0°.38, while the more frequent variations were between 0°.15 and 0°.30. The temperature of the air space above the water, in which the manometers were located, was always higher and much more variable. The difference, however, rarely exceeded 1°.0, except temporarily, after the opening of the bath. The generally higher and more fluctuating temperature of the air in the bath was due, of course, to the higher and rapidly changing temperature of the external air. The weather conditions under which the work was done were so unfavorable in these respects that the highest speed of the air pump did not suffice to maintain a constant relation between the temperature of the water and that of the air within the bath.

The material employed for the measurements was, as on former occasions, the purest obtainable "rock candy." It left no ash when burned, and gave no reaction for invert sugar with Fehling's solution. In this instance the usual determination of carbon and hydrogen was omitted, but not that with the polariscope. The standard solution[1] (containing 26.003 grams of sugar in 100 cc. at 17°.5) gave a rotation of 99.95, instead of 100, saccharimetric degrees.

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[1] THIS JOURNAL, 36, 1.

The details of the individual measurements are presented in the following tables.

Tables I. to XXVII. give the record of the individual experiments in this (the III.) series of measurements of the osmotic pressure of cane sugar solutions. As in previous papers, no essential data have been omitted except the actual readings with the telescope. This is believed to be the proper course, because hereafter questions of interpretation will arise which cannot be adequately discussed unless all the essential quantitative facts pertaining to the measurements are within reach.

The results have been brought together, for convenience of examination, in Table XXVIII. and in Table XXIX. they have been summarized for each concentration of solution.

It will be noticed that every solution suffered some loss of rotation while in the cell, and that this loss has been interpreted and recorded in the tables (I. to XXVII.) as due to *inversion* of the cane sugar. It had been established on previous occasions[2] not only that inversion does always take place in the cell, but that such inversion exceeds that which occurs within the same time in identical solutions which are not enclosed in the osmotic cell.

We have been perfectly aware, however, that not all the loss of rotation is due to inversion, that in every case, in fact, a considerable portion of it results from a dilution of the solution in the cell which occurs while the cell is being closed at the beginning, and opened at the end, of an experiment, and also formerly, from a slipping of the manometer in the stopper or a crowding upwards of both manometer and stopper under the pressure of the cell contents, either of which movements increases the capacity of the cell and necessarily brings about

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[1] Landolt, Das Optische Drehungsvermögen, p. 335.

[2] THIS JOURNAL, **34**, 30; **36**, 41.

Table I.

Original wt. normal concentration of solution, 0.1.
Rotation of original solution, $12^\circ.5$ ($t = 22^\circ$).
Rotation at conclusion of exp't, $12^\circ.3$ ($t = 22^\circ$).
Loss in rotation, $0^\circ.2$ = 1.60 per cent.
Calibration units of air in manometer, 476.96.
Time of setting up cell, 12.00 noon, Dec. 14, 1906.

Experiment No. 1
Manometer used, No. 18.
Capillary depression, 0.02.
Cell used, B.
Resistance of membrane, 137,500.
Initial pressure. 1.74 atmospheres.

	Temperature.		Volume of air in manometer.		Corrections.						
Time.	Solution.	Air in manometer.	Uncorrected.	Corrected.	Atmospheric pressure.	Liquids in manometer.	Inversion.	Capillary depression.	Osmotic pressure corrected.	Theoretical gas pressure.	Difference between pressure found and calculated.
Dec. 14.											
1.10 P.M.	$0^\circ.22$	$4^\circ.1$									
4.20 "	$0^\circ.18$	$0^\circ.55$									
8.00 "	$0^\circ.20$	$0^\circ.52$	159.50	159.20	1.01	0.43	0.03	0.02	2.41	2.23	+0.18
11.00 "	$0^\circ.18$	$0^\circ.56$	159.39	159.06	1.01	0.43	0.03	0.02	2.41	2.23	+0.18
Dec. 15.											
10.45 A.M.	$0^\circ.28$	$0^\circ.65$	159.37	158.99	1.00	0.43	0.03	0.02	2.42	2.23	+0.19
12.30 P.M.	$0^\circ.30$	$0^\circ.84$	159.40	158.90	1.00	0.43	0.03	0.02	2.42	2.23	+0.19
4.00 "	$0^\circ.36$	$0^\circ.91$	159.42	158.92	1.00	0.43	0.03	0.02	2.42	2.23	+0.19

Displacement of the manometer = 0.07 mm.

Table II.

Original wt. normal concentration of solution, 0.1.
Rotation of original solution, 12°.5 ($t = 20°$).
Rotation at conclusion of exp't, 12°.4 ($t = 20°$).
Loss in rotation, 0°.1 = 0.80 per cent.
Calibration units of air in manometer, 476.96.
Time of setting up cell, 3.30 P. M., Dec. 17, 1906.

Experiment No. 2.
Manometer used, No. 18.
Capillary depression, 0.02.
Cell used, B.
Resistance of membrane, 136,000.
Initial pressure, 2.09 atmospheres.

Time.	Temperature.		Volume of air in manometer.		Corrections.				Osmotic pressure corrected.	Theoretical gas pressure.	Difference between pressure found and calculated.
	Solution.	Air in manometer.	Uncorrected.	Corrected.	Atmospheric pressure.	Liquids in manometer.	Inversion.	Capillary depression.			
Dec. 17.											
5.00 P.M.	0°.23	3°.00									
7.30 "	0°.22	0°.80									
11.45 "	0°.14	0°.69	159.48	159.08	1.00	0.43	0.01	0.02	2.44	2.23	+0.21
Dec. 18.											
10.00 A.M.	0°.26	0°.59	158.71	158.37	1.01	0.43	0.01	0.02	2.44	2.23	+0.21
12.45 P.M.	0°.22	0°.56	158.66	158.33	1.01	0.43	0.01	0.02	2.44	2.23	+0.21
4.00 "	0°.22	0°.56	158.59	158.26	1.01	0.43	0.01	0.02	2.44	2.23	+0.21

Displacement of the manometer = 0.07 mm.

Table III.

Original wt. normal concentration of solution, 0.1.
Rotation of original solution, 12°.65 (t = 18°.5).
Rotation at conclusion of exp't, 12°.60 (t = 18°.5).
Loss in rotation, 0°.05 = 0.39 per cent.
Calibration units of air in manometer, 434.93.
Time of setting up cell, 3.30 P. M., Jan. 11, 1907.

Experiment No. 3.
Manometer used No. 13.
Capillary depression, 0.02.
Cell used, B.
Resistance of membrane, 122,000.
Initial pressure, 1.64 atmospheres.

	Temperature.		Volume of air in manometer.		Corrections.						
Time.	Solution.	Air in manometer.	Uncorrected.	Corrected.	Atmospheric pressure.	Liquids in manometer.	Inversion.	Capillary depression.	Osmotic pressure corrected.	Theoretical gas pressure.	Difference between pressure found and calculated.
Jan. 11.											
4.45 P.M.	0°.24	3°.00	205.93	205.12							
11.30 "	0°.14	0°.89	152.39	151.88	1.00	0.48	0.01	0.02	2.36	2.23	+0.13
Jan. 12.											
10.30 A.M.	0°.14	0°.95	152.08	151.55	1.00	0.48	0.01	0.02	2.36	2.23	+0.13
1.00 P.M.	0°.24	1°.12	152.15	151.52	0.99	0.48	0.01	0.02	2.37	2.23	+0.14
4.30 "	0°.24	1°.20	152.10	151.44	0.99	0.48	0.01	0.02	2.37	2.23	+0.14
7.30 "	0°.28	1°.30	152.11	151.39	1.00	0.48	0.01	0.02	2.36	2.23	+0.13
Jan. 13.											
10.15 "	0°.38	1°.17	151.11	150.46	1.01	0.48	0.01	0.02	2.37	2.23	+0.14

Displacement of the manometer = 0.09 mm.

Table IV.

Original wt. normal concentration of solution, 0.1.
Rotation of original solution, 12°.65 (t = 18°.5).
Rotation at conclusion of exp't, 12°.55 (t = 18°.5).
Loss in rotation, 0°.1 = 0.79 per cent.
Calibration units of air in manometer, 396.89.
Time of setting up cell, 4.00 P. M., Jan. 11, 1907.

Experiment No. 4.
Manometer used, No. 6.
Capillary depression, 0.02.
Cell used, A.
Resistance of membrane, 157,000.
Initial pressure, 1.34 atmospheres.

	Temperature.		Volume of air in manometer.		Corrections.						
Time.	Solution.	Air in manometer.	Uncorrected.	Corrected.	Atmospheric pressure.	Liquids in manometer.	Inversion.	Capillary depression.	Osmotic pressure corrected.	Theoretical gas pressure.	Difference between pressure found and calculated.
Jan. 11.											
4.45 P.M.	0°.24	3°.00	219.57								
11.30 "	0°.14	0°.89	160.90	160.38							
Jan. 12.											
10.30 A.M.	0°.14	0°.95	139.62	139.14	1.00	0.49	0.01	0.02	2.37	2.23	+0.14
1.00 P.M.	0°.24	1°.12	139.58	139.02	0.99	0.49	0.01	0.02	2.38	2.23	+0.15
4.30 "	0°.24	1°.20	139.43	138.82	0.99	0.49	0.01	0.02	2.39	2.23	+0.16
7.30 "	0°.28	1°.30	139.31	138.65	1.00	0.49	0.01	0.02	2.38	2.23	+0.15
Jan. 13.											
10.15 A.M.	0°.38	1°.17	138.58	137.99	1.01	0.49	0.01	0.02	2.39	2.23	+0.16

Displacement of the manometer = 0.09 mm.

Table V.

Original wt. normal concentration of solution, 0.2.
Rotation of original solution, 24°.75 ($t = 21°$).
Rotation at conclusion of exp't, 24°.60 ($t = 21°$).
Loss in rotation, 0°.15 = 0.61 per cent.
Calibration units of air in manometer, 476.96.
Time of setting up cell, 4.00 P. M., Dec. 19, 1906.

Experiment No. 1.
Manometer used, No. 18.
Capillary depression, 0.02.
Cell used, B.
Resistance of membrane, 124,000.
Initial pressure, 4.09 atmospheres.

Time.	Temperature.		Volume of air in manometer.		Corrections.				Osmotic pressure corrected.	Theoretical gas pressure.	Difference between pressure found and calculated.
	Solution.	Air in manometer.	Uncorrected.	Corrected.	Atmospheric pressure.	Liquids in manometer.	Inversion.	Capillary depression.			
Dec. 19.											
5.30 P.M.	0°.13	2°.30									
7.30 "	0°.14	0°.87									
11.00 "	0°.16	0°.69	91.35	91.12	1.01	0.52	0.02	0.02	4.74	4.46	+0.28
Dec. 20.											
10.00 A.M.	0°.20	0°.77	91.27	91.01	1.00	0.52	0.02	0.02	4.76	4.46	+0.30
12.45 P.M.	0°.24	0°.88	91.35	91.06	0.99	0.52	0.02	0.02	4.77	4.46	+0.31
3.30 "	0°.26	0°.91	91.32	91.02	0.99	0.52	0.02	0.02	4.77	4.46	+0.31

Displacement of the manometer = 0.05 mm.

Table VI.

Original wt. normal concentration of solution, 0.2.
Rotation of original solution, 24°.8 ($t = 21°$).
Rotation at conclusion of exp't, 24°.65 ($t = 21°$).
Loss in rotation, 0°.15 = 0.60 per cent.
Calibration units of air in manometer, 476.96.
Time of setting up cell, 4.00 P. M., Dec. 21, 1906.

Experiment No. 2.
Manometer used, No. 18.
Capillary depression, 0.02.
Cell used, B.
Resistance of membrane, 122,000.
Initial pressure, 3.79 atmospheres.

	Temperature.		Volume of air in manometer.		Corrections.						
Time.	Solution.	Air in manometer.	Uncorrected.	Corrected.	Atmospheric pressure.	Liquids in manometer.	Inversion.	Capillary depression.	Osmotic pressure corrected.	Theoretical gas pressure.	Difference between pressure found and calculated.
Dec. 21.											
5.30 P.M.	0°.26	2°.40									
7.30 "	0°.28	1°.05									
10.00 "	0°.28	0°.99	91.90	91.57	0.99	0.52	0.02	0.02	4.74	4.46	+0.28
Dec. 22.											
9.30 A.M.	0°.28	0°.82	91.57	91.30	0.99	0.52	0.02	0.02	4.75	4.46	+0.29
1.00 P.M.	0°.32	0°.85	91.48	91.20	0.99	0.52	0.02	0.02	4.76	4.46	+0.30
5.00 "	0°.31	0°.95	91.49	91.17	0.99	0.52	0.02	0.02	4.76	4.46	+0.30

Displacement of the manometer = 0.05 mm.

Table VII.

Original wt. normal concentration of solution, 0.3.
Rotation of original solution, 36°.6 ($t = 22°$).
Rotation at conclusion of exp't, 36°.1 ($t = 22°$).
Loss in rotation, 0°.5 = 1.37 per cent.
Calibration units of air in manometer, 471.37.
Time of setting up cell, 4.00 P. M., Dec. 5, 1906.

Experiment No. 1.
Manometer used, No. 21.
Capillary depression, 0.02.
Cell used, B.
Resistance of membrane, 158,000
Initial pressure, 5.01 atmospheres.

Time.	Temperature.		Volume of air in manometer.		Corrections.				Osmotic pressure corrected.	Theoretical gas pressure.	Difference between pressure found and calculated.
	Solution.	Air in manometer.	Uncorrected.	Corrected.	Atmospheric pressure.	Liquids in manometer.	Inversion.	Capillary depression.			
Dec. 5.											
5.30 P.M.	0°.16	1°.93									
9.30 "	0°.14	0°.59									
Dec. 6.											
10.00 A.M.	0°.18	0°.70	63.30	63.14	0.99	0.58	0.07	0.02	7.01	6.68	+0.33
12.30 P.M.	0°.22	0°.89	63.27	63.07	0.98	0.58	0.07	0.02	7.02	6.68	+0.34
5.00 "	0°.30	1°.08	63.31	63.06	0.98	0.58	0.07	0.02	7.02	6.69	+0.33
10.30 "	0°.33	1°.00	63.33	63.10	0.99	0.58	0.07	0.02	7.01	6.69	+0.32
Dec. 7.											
10.00 A.M	0°.34	0°.70	63.12	62.96	1.00	0.58	0.07	0.02	7.02	6.69	+0.33
12.50 P.M.	0°.33	0°.74	63.14	62.97	1.00	0.58	0.07	0.02	7.02	6.69	+0.33
4.10 "	0°.34	0°.64	63.15	63.00	1.00	0.58	0.07	0.02	7.01	6.69	+0.32

Displacement of the manometer = 0.06 mm.

Table VIII.

Original wt. normal concentration of solution, 0.03.
Rotation of original solution, 36°.6 ($t = 20°$).
Rotation at conclusion of exp't, 36°.0 ($t = 20°$).
Loss in rotation, 0°.6 = 1.64 per cent.
Calibration units of air in manometer, 476.96.
Time of setting up cell, 4.00 P. M., Dec. 11, 1906.

Experiment No. 2.
Manometer used, No. 18.
Capillary depression, 0.02.
Cell used, B.
Resistance of membrane, 122,000.
Initial pressure, 5.79 atmospheres.

	Temperature.		Volume of air in manometer.		Corrections.						
Time.	Solution.	Air in manometer.	Uncorrected.	Corrected.	Atmospheric pressure.	Liquids in manometer.	Inversion.	Capillary depression.	Osmotic pressure corrected.	Theoretical gas pressure.	Difference between pressure found and calculated.
Dec. 11.											
5.30 P.M.	0°.16	1°.54									
9.15 "	0°.16	0°.44									
Dec. 12.											
12.10 A.M.	0°.15	0°.36	63.43	63.34	1.01	0.56	0.08	0.02	7.02	6.68	+0.34
10.00 "	0°.14	0°.29	63.35	63.28	1.02	0.56	0.08	0.02	7.02	6.68	+0.34
12.50 P.M.	0°.14	0°.37	63.35	63.27	1.01	0.56	0.08	0.02	7.03	6.68	+0.35
3.50 "	0°.18	0°.53	63.36	63.24	1.01	0.56	0.08	0.02	7.03	6.68	+0.35

Displacement of the manometer = 0.06 mm.

Table IX.

Original wt. normal concentration of solution, 0.4.
Rotation of original solution, 47°.85 (t = 22°).
Rotation at conclusion of exp't, 47°.30 (t = 22).
Loss in rotation, 0°.55 = 1.15 per cent.
Calibration units of air in manometer, 434.93.
Time of setting up cell, 4.00 P. M., Dec. 26, 1906.

Experiment No. 1.
Manometer used, No. 13.
Capillary depression, 0.02.
Cell used, B.
Resistance of membrane, 140,000.
Initial pressure, 7.73 atmospheres.

Time.	Temperature.		Volume of air in manometer.		Corrections.						
	Solution.	Air in manometer.	Uncorrected.	Corrected.	Atmospheric pressure.	Liquids in manometer.	Inversion.	Capillary depression.	Osmotic pressure corrected.	Theoretical gas pressure.	Difference between pressure found and calculated.
Dec. 26.											
5.00 P.M.	0°.18	3°.30	54.32								
8.00 "	0°.16	0°.75	45.32								
11.00 "	0°.16	0°.63	44.88	44.78	1.00	0.62	0.08	0.02	9.27	8.91	+0.36
Dec. 27.											
9.45 A.M.	0°.16	0°.57	44.78	44.69	1.00	0.62	0.08	0.02	9.29	8.91	+0.38
12.30 P.M.	0°.20	0°.71	44.80	44.69	1.00	0.62	0.08	0.02	9.29	8.91	+0.38
4.00 "	0°.22	0°.79	44.79	44.66	0.99	0.62	0.08	0.02	9.31	8.91	+0.40

Displacement of the manometer = 0.08 mm.

Table X.

Original wt. normal concentration of solution, 0.4.
Rotation of original solution, 48°.0 (t = 20°).
Rotation at conclusion of exp't, 47°.4 (t = 20°).
Loss in rotation, 0°.6 (1.25 per cent).
Calibration units of air in manometer, 396.89.
Time of setting up cell, 4.00 P. M., Dec. 28, 1906.

Experiment No. 2.
Manometer used, No. 6.
Capillary depression, 0.02.
Cell used, B.
Resistance of membrane, 124,444.
Initial pressure, 6.60 atmospheres.

Time.	Temperature.		Volume of air in manometer.		Corrections.				Osmotic pressure corrected.	Theoretical gas pressure.	Difference between pressure found and calculated.
	Solution.	Air in manometer.	Uncorrected.	Corrected.	Atmospheric pressure.	Liquids in manometer.	Inversion.	Capillary depression.			
Dec. 28.											
5.00 P.M.	0°.22	3°.5	57.85								
7.30 "	0°.23	1°.07									
11.15 "	0°.22	1°.04	41.24	41.08	1.00	0.65	0.08	0.02	9.25	8.91	+0.34
Dec. 29.											
9.15 A.M.	0°.26	1°.03	41.24	41.08	1.00	0.65	0.08	0.02	9.25	8.92	+0.33
1.00 P.M.	0°.33	1°.17	41.22	41.04	1.00	0.65	0.08	0.02	9.26	8.92	+0.34
4.00 "	0°.32	1°.26	41.23	41.04	1.00	0.65	0.08	0.02	9.26	8.92	+0.34

Displacement of the manometer = 0.07 mm.

Table XI.

Original wt. normal concentration of solution, 0.4.
Rotation of original solution, 48°.0 (t = 20°).
Rotation at conclusion of exp't, 47°.6 (t = 20°).
Loss in rotation, 0°.4 = 0.83 per cent.
Calibration units of air in manometer, 434.98.
Time of setting up cell, 3.30 P. M., Jan. 5, 1907.

Experiment No. 3.
Manometer used, No. 5.
Capillary depression, 0.02.
Cell used, B.
Resistance of membrane, 136,600.
Initial pressure, 7.57 atmospheres.

Time.	Temperature.		Volume of air in manometer.		Corrections.				Osmotic pressure corrected.	Theoretical gas pressure.	Difference between pressure found and calculated.
	Solution.	Air in manometer.	Uncorrected.	Corrected.	Atmospheric pressure.	Liquids in manometer.	Inversion.	Capillary depression.			
Jan. 5.											
5.15 P.M.	0°.26	3°.00	55.49								
8.00 "	0°.18	1°.18	45.56								
12.00 "	0°.20	0°.97	45.23								
Jan. 6.											
10.00 A.M.	0°.22	0°.85	45.21								
2.45 P.M.	0°.24	0°.96	45.21								
7.30 "	0°.26	1°.01	45.04	44.87	1.00	0.63	0.06	0.02	9.28	8.92	+0.36
Jan. 7.											
10.15 A.M.	0°.32	1°.17	45.00	44.81	1.01	0.63	0.06	0.02	9.29	8.92	+0.37
12.30 P.M.	0°.34	1°.39	44.99	44.76	1.00	0.63	0.06	0.02	9.31	8.92	+0.39
3.45 "	0°.34	1°.54	45.01	44.75	1.00	0.63	0.06	0.02	9.31	8.92	+0.39

Displacement of the manometer = 0.22 mm.

Table XII.

Original wt. normal concentration of solution, 0.4.
Rotation of original solution, 48°.0 (t = 20°.5).
Rotation at conclusion of exp't, 47°.6 (t = 20°.5).
Loss in rotation, 0.4 = 0.83 per cent.
Calibration units of air in manometer, 396.89.
Time of setting up cell, 4.00 P. M., Jan. 9, 1907.

Experiment No. 4.
Manometer used, No. 6.
Capillary depression, 0.02.
Cell used, D.
Resistance of membrane, 93,000.
Initial pressure, 8.08 atmospheres.

	Temperature.		Volume of air in manometer.		Corrections.						
Time.	Solution.	Air in manometer.	Uncorrected.	Corrected.	Atmospheric pressure.	Liquids in manometer.	Inversion.	Capillary depression.	Osmotic pressure corrected.	Theoretical gas pressure.	Difference between pressure found and calculated.
Jan. 9.											
5.30 P.M.	0°.22	3°.30	47.68								
7.30 "	0°.16	0°.89	41.51	41.37							
10.30 "	0°.14	0°.77	41.28	41.16	1.00	0.65	0.06	0.02	9.25	8.91	+0.34
Jan. 10.											
10.00 A.M.	0°.16	0°.64	41.27	41.17	1.00	0.65	0.06	0.02	9.25	8.91	+0.34
1.00 P.M.	0°.16	0°.72	41.28	41.17	1.00	0.65	0.06	0.02	9.25	8.91	+0.34
4.00 "	0°.12	0°.81	41.28	41.16	0.99	0.65	0.06	0.02	9.26	8.91	+0.35

Displacement of the manometer = 0.04 mm.

Table XIII.

Original wt. normal concentration of solution, 0.5.
Rotation of original solution, 58°.7 (t = 19°.5).
Rotation at conclusion of exp't, 57°.8 (t = 19°.5).
Loss in rotation, 0°.9 = 1.53 per cent.
Calibration units of air in manometer, 471.37.
Time of setting up cell, 5.00 P. M., Nov. 26, 1906.

Experiment No. 1.
Manometer used, No. 21.
Capillary depression, 0.02.
Cell used, G.
Resistance of membrane, 58,947.
Initial pressure, 11.03 atmospheres.

Time.	Temperature.		Volume of air in manometer.		Corrections.				Osmotic pressure corrected.	Theoretical gas pressure.	Difference between pressure found and calculated.
	Solution.	Air in manometer.	Uncorrected.	Corrected.	Atmospheric pressure.	Liquids in manometer.	Inversion.	Capillary depression.			
Nov. 26.											
7.30 P.M.	0°.24	1°.88									
11.10 "	0°.26	1°.69									
Nov. 27.											
10.10 A.M.	0°.33	1°.80	39.46	39.20	1.00	0.61	0.13	0.02	11.53	11.14	+0.39
12.40 P.M.	0°.38	1°.99	39.50	39.21	1.00	0.61	0.13	0.02	11.52	11.15	+0.37
3.30 "	0°.38	2°.03	39.48	39.19	1.00	0.61	0.13	0.02	11.53	11.15	+0.38
7.30 "	0°.16	1°.29	39.36	39.18	1.01	0.61	0.13	0.02	11.52	11.14	+0.38
11.15 "	0°.14	1°.20	39.28	39.11	1.00	0.61	0.13	0.02	11.56	11.14	+0.42
Nov. 28.											
10.00 A.M.	0°.18	1°.33	39.36	39.17	1.00	0.61	0.13	0.02	11.54	11.14	+0.40

Displacement of the manometer = 0.24 mm.

Table XIV.

Original wt. normal concentration of solution, 0.5.
Rotation of original solution, 58°.75 (t = 18°.5).
Rotation at conclusion of exp't, 57°.75 (t = 18°.5).
Loss in rotation, 1°.00 = 1.70 per cent.
Calibration units of air in manomter, 471.37.
Time of setting up cell, 12.30 P. M., Nov. 30, 1906.

Experiment No. 2.
Manometer used, No. 21.
Capillary depression, 0.02.
Cell used, G.
Resistance of membrane, 135,000.
Initial pressure, 11.39 atmospheres.

Time.	Temperature.		Volume of air in manometer.		Corrections.				Osmotic pressure corrected.	Theoretical gas pressure.	Difference between pressure found and calculated.
	Solution.	Air in manometer.	Uncorrected.	Corrected.	Atmospheric pressure.	Liquids in manometer.	Inversion.	Capillary depression.			
Nov. 30.											
3.30 P.M.	0°.22	0°.77									
7.30 "	0°.20	0°.69									
11.00 "	0°.20	0°.69	39.19	39.09	1.00	0.61	0.14	0.02	11.55	11.14	+0.41
Dec. 1.											
9.15 A. M.	0°.26	0°.76	39.05	38.94	1.00	0.61	0.14	0.02	11.60	11.14	+0.46
12.40 P.M.	0°.22	0°.81	39.03	38.91	1.00	0.61	0.14	0.02	11.61	11.14	+0.47
4.00 "	0°.22	0°.79	39.04	38.93	1.00	0.61	0.14	0.02	11.60	11.14	+0.46

Displacement of the manometer = 0.22.

Table XV.

Original wt. normal concentration of solution, 0.5.
Rotation of original solution, 58°.80 ($t = 20°$).
Rotation at conclusion of exp't, 57°.75 ($t = 20°$).
Loss in rotation, 1°.05 = 1.71 per cent.
Calibration units of air in manometer, 476.96.
Time of setting up cell, 3.30 P. M., Dec. 3, 1906.

Experiment No. 3.
Manometer used, No. 18.
Capillary depression, 0.02.
Cell used, G.
Resistance of membrane, 110,000.
Initial pressure, 11.30 atmospheres.

Time.	Temperature.		Volume of air in manometer.		Corrections.				Osmotic pressure corrected.	Theoretical gas pressure.	Difference between pressure found and calculated.
	Solution.	Air in manometer.	Uncorrected.	Corrected.	Atmospheric pressure.	Liquids in manometer.	Inversion.	Capillary depression.			
Dec. 3											
5.20 P.M.	0°.16	5°.00									
7.45 "	0°.16	0°.66									
11.15 "	0°.14	0°.39									
Dec. 4											
10.20 A.M.	0°.12	0°.20	39.10	39.07	1.01	0.59	0.15	0.02	11.65	11.14	+0.51
12.45 P.M.	0°.12	0°.25	39.13	39.09	1.01	0.59	0.15	0.02	11.65	11.14	+0.51
3.45 "	0°.12	0°.33	39.17	39.12	1.01	0.59	0.15	0.02	11.64	11.14	+0.50
7.45 "	0°.14	0°.39	39.17	39.11	1.00	0.59	0.15	0.02	11.65	11.14	+0.51
11.00 "	0°.15	0°.40	39.16	39.10	1.01	0.59	0.15	0.02	11.64	11.14	+0.50
Dec. 5											
10.10 A.M.	0°.18	0°.38	39.15	39.09	1.01	0.59	0.15	0.02	11.65	11.14	+0.51
4.15 P.M.	0°.18	0°.52	39.18	39.11	1.00	0.59	0.15	0.02	11.65	11.14	+0.51

Displacement of the manometer = 0.07.

Table XVI.

Original wt. normal concentration of solution, 0.5.
Rotation of original solution, 58°.85 ($t = 20°$).
Rotation at conclusion of exp't, 58°.10 ($t = 20°$).
Loss in rotation, 0°.75 = 1.29 per cent.
Calibration units of air in manometer, 465.78.
Time of setting up cell, 4.30 P. M., Jan. 4, 1907.

Experiment No. 4.
Manometer used, No. 11.
Capillary depression, 0.02.
Cell used, D.
Resistance of membrane, 90,000.
Initial pressure, 8.13 atmospheres.

Time.	Temperature.		Volume of air in manometer.		Corrections.				Osmotic pressure corrected.	Theoretical gas pressure.	Difference between pressure found and calculated.
	Solution.	Air in manometer.	Uncorrected.	Corrected.	Atmospheric pressure.	Liquids in manometer.	Inversion.	Capillary depression.			
Jan. 4											
5.15 P.M.	0°.26	2°.10	54.70								
8.00 "	0°.16	1°.07	38.70								
10.45 "	0°.16	0°.97	38.31	38.17	1.00	0.56	0.11	0.02	11.67	11.14	+0.53
Jan. 5											
10.30 A.M.	0°.18	0°.89	38.24	38.12	1.01	0.56	0.11	0.02	11.68	11.14	+0.54
1.00 P.M.	0°.20	1°.09	38.28	38.13	1.00	0.56	0.11	0.02	11.69	11.14	+0.55
4.00 "	0°.26	1°.26	38.31	38.12	1.00	0.56	0.11	0.02	11.69	11.14	+0.55

Displacement of the manometer = 0.38 mm.

Table XVII.

Original wt. normal concentration of solution, 0.6.
Rotation of original solution, 69°.4 ($t = 19°$).
Rotation at conclusion of exp't, 68°.2 ($t = 19°$).
Loss in rotation, 1°.2 = 1.73 per cent.
Calibration units of air in manometer, 434.93.
Time of setting up cell, 4.30 P. M., Dec. 31, 1906.

Experiment No. 1.
Manometer used, No. 13.
Capillary depression, 0.02.
Cell used, B.
Resistance of membrane, 161,000.
Initial pressure, 12.08.

Time.	Temperature.		Volume of air in manometer.		Corrections.				Osmotic pressure corrected.	Theoretical gas pressure.	Difference between pressure found and calculated.
	Solution.	Air in manometer.	Uncorrected.	Corrected.	Atmospheric pressure.	Liquids in manometer.	Inversion.	Capillary depression.			
Dec. 31.											
6.00 P.M.	0°.22	2°.00	35.26								
11.00 "	0°.16	1°.34	30.19	30.04	1.00	0.64	0.12	0.02	14.02	13.37	+0.65
Jan. 1, '07											
10.00 A.M.	0°.22	1°.20	30.19	30.06	1.00	0.64	0.12	0.02	14.01	13.37	+0.64
12.30 P.M.	0°.22	1°.29	30.19	30.05	1.00	0.64	0.12	0.02	14.01	13.37	+0.64
5.30 "	0°.24	1°.28	30.21	30.07	1.01	0.64	0.12	0.02	13.99	13.37	+0.62
7.30 "	0°.28	1°.43	30.24	30.08	1.01	0.64	0.12	0.02	13.99	13.37	+0.62
11.00 "	0°.25	1°.36	30.24	30.09	1.01	0.64	0.12	0.02	13.98	13.37	+0.61
Jan. 2, '07											
9,30 A.M.	0°.24	1°.10	30.18	30.06	1.01	0.64	0.12	0.02	14.00	13.37	+0.63

Displacement of the manometer = 0.48 mm.

Table XVIII.

Original wt. normal concentration of solution, 0.6.
Rotation of original solution, 69°.35 ($t = 20°$).
Rotation at conclusion of exp't, 68°.05 ($t = 20°$).
Loss in rotation, 1°.30 = 1.86 per cent.
Calibration units of air in manometer, 369.89.
Time of setting up cell, 4.00 P. M., Jan. 2, 1907.

Experiment No. 2.
Manometer used, No. 6.
Capillary depression, 0.02.
Cell used, G.
Resistance of membrane, 102,000.
Initial pressure, 13.09.

	Temperature.		Volume of air in manometer.		Corrections.						
Time.	Solution.	Air in manometer.	Uncorrected.	Corrected.	Atmospheric pressure.	Liquids in manometer.	Inversion.	Capillary depression.	Osmotic pressure corrected.	Theoretical gas pressure.	Difference between pressure found and calculated.
Jan. 2.											
5.00 P.M.	0°.24	3°.3	29.97								
8.00 "	0°.20	1°.01	27.63	27.53	1.01	0.67	0.14	0.02	13.96	13.37	+0.59
10.30 "	0°.20	0°.94	27.60	27.51	1.01	0.67	0.14	0.02	13.97	13.37	+0.60
Jan. 3											
10.15 A.M.	0°.20	0°.84	27.63	27.55	1.01	0.67	0.14	0.02	13.95	13.37	+0.58
1.00 P.M.	0°.22	0°.92	27.60	27.51	1.01	0.67	0.14	0.02	13.97	13.37	+0.60
4.15 "	0°.25	0°.95	27.59	27.49	1.01	0.67	0.14	0.02	13.98	13.37	+0.61

Displacement of the manometer = 0.10 mm.

Table XIX.

Original wt. normal concentration of solution, 0.7.
Rotation of original solution, 79°.3 (t = 20°).
Rotation at conclusion of exp't, 78°.1 (t = 20°).
Loss in rotation, 1°.2 = 1.51 per cent.
Calibration units of air in manometer, 434.93.
Time of setting up cell, 4.00 P.M., Jan. 3, 1907.

Experiment No. 1.
Manometer used, No. 13.
Capillary depression, 0.02.
Cell used, B.
Resistance of membrane, 159,300.
Initial pressure, 13.53.

Time.	Temperature.		Volume of air in manometer.		Corrections.				Osmotic pressure corrected.	Theoretical gas pressure.	Difference between pressure found and calculated.
	Solution.	Air in manometer.	Uncorrected.	Corrected.	Atmospheric pressure.	Liquids in manometer.	Inversion.	Capillary depression.			
Jan. 3.											
5.15 P.M.	0°.18	2°.80	31.68								
8.15 “	0°.16	0°.91	25.85								
10.45 “	0°.16	0°.93	25.74	25.65	1.00	0.65	0.18	0.02	16.45	15.60	+0.85
Jan. 4											
10.00 A.M.	0°.26	1°.29	25.73	25.61	0.99	0.65	0.18	0.02	16.48	15.60	+0.88
12.45 P.M.	0°.30	1°.38	25.75	25.62	0.99	0.65	0.18	0.02	16.48	15.60	+0.88
4.15 “	0°.32	1°.19	25.74	25.64	1.00	0.65	0.18	0.02	16.46	15.60	+0.86

Displacement of the manometer = 0.61 mm.

Table XX.

Original wt. normal concentration of solution, 0.7.
Rotation of original solution, 79°.3 ($t = 20^\circ$).
Rotation at conclusion of exp't, 78°.2 ($t = 20^\circ$).
Loss in rotation, 1°.1 = 1.39 per cent.
Calibration units of air in manometer, 396.89.
Time of setting up cell, 1.30 P. M., Jan. 18, 1907.

Experiment No. 2.
Manometer used, No. 6.
Capillary depression, 0.02.
Cell used, D.
Resistance of membrane, 111,500.
Initial pressure, 13.84 atmospheres.

Time.	Temperature.		Volume of air in manometer.		Corrections.				Osmotic pressure corrected.	Theoretical gas pressure.	Difference between pressure found and calculated.
	Solution.	Air in manometer.	Uncorrected.	Corrected.	Atmospheric pressure.	Liquids in manometer.	Inversion.	Capillary depression.			
Jan. 18											
1.15 P.M.	0°.16	4°.5	28.51								
5.15 "	0°.14	0°.59	23.37	23.32	1.00	0.67	0.16	0.02	16.55	15.60	+0.95
7.30 "	0°.16	0°.83	23.40	23.33	1.00	0.67	0.16	0.02	16.54	15.60	+0.94
11.45 "	0°.14	0°.76	23.37	23.31	1.00	0.67	0.16	0.02	16.56	15.60	+0.96
Jan. 19											
10.30 A.M.	0°.16	0°.71	23.41	23.35	1.00	0.67	0.16	0.02	16.53	15.60	+0.93

Displacement of the manometer = 0.45 mm.

Table XXI.

Original wt. normal concentration of solution, 0.8.
Rotation of original solution, 89°.15 ($t = 20^\circ$).
Rotation at conclusion of exp't, 87°.60 ($t = 20^\circ$).
Loss in rotation, 1°.55 = 1.74 per cent.
Calibration units of air in manometer, 396.89.
Time of setting up cell, 4.00 P. M., Jan. 4, 1907.

Experiment No. 1.
Manometer used, No. 6.
Capillary depression, 0.02.
Cell used, G.
Resistance of membrane, 112,000.
Initial pressure, 17.64 atmospheres.

	Temperature.		Volume of air in manometer.		Corrections.						
Time.	Solution.	Air in manometer.	Uncorrected.	Corrected.	Atmospheric pressure.	Liquids in manometer.	Inversion.	Capillary depression.	Osmotic pressure corrected.	Theoretical gas pressure.	Difference between pressure found and calculated.
Jan. 4											
5.15 P.M.	0°.26	2°.10	22.28								
8.00 "	0°.16	1°.07	20.54								
10.45 "	0°.16	0°.97	20.43	20.36	1.00	0.68	0.23	0.02	18.96	17.82	+1.14
Jan. 5											
10.30 A.M.	0°.18	0°.89	20.46	20.39	1.01	0.68	0.23	0.02	18.92	17.82	+1.01
1.00 P.M.	0°.20	1°.09	20.49	20.41	1.00	0.68	0.23	0.02	18.92	17.82	+1.10
4.00 "	0°.26	1°.26	20.50	20.41	1.00	0.68	0.23	0.02	18.92	17.83	+1.09

Displacement of the manometer = 0.01 mm.

Table XXII.

Original wt. normal concentration of solution, 0.8.
Rotation of original solution, $89^\circ.0$ ($t = 20^\circ.5$).
Rotation at conclusion of exp't, $87^\circ.4$ ($t = 20^\circ.5$).
Loss in rotation, $1^\circ.6$ = 1.80 per cent.
Calibration units of air in manometer, 396.89.
Time of setting up cell, 4.15 P. M., Jan. 14, 1907.

Experiment No. 2.
Manometer used, No. 6.
Capillary depression, 0.02.
Cell used, G.
Resistance of membrane, 110,000.
Initial pressure, 17.68 atmospheres.

Time.	Temperature.		Volume of air in manometer.		Corrections.				Osmotic pressure corrected.	Theoretical gas pressure.	Difference between pressure found and calculated.
	Solution.	Air in manometer.	Uncorrected.	Corrected.	Atmospheric pressure.	Liquids in manometer.	Inversion.	Capillary depression.			
Jan. 14.											
6.00 P.M.	$0^\circ.22$	$2^\circ.60$	22.27								
7.30 "	$0^\circ.16$	$1^\circ.19$	20.60	20.51	1.00	0.67					
11.00 "	$0^\circ.16$	$1^\circ.00$	20.47	20.40	1.00	0.67	0.24	0.02	18.91	17.82	+1.09
Jan. 15											
10.15 A.M.	$0^\circ.22$	$0^\circ.96$	20.49	20.42	1.00	0.67	0.24	0.02	18.89	17.82	+1.07
1.00 P.M.	$0^\circ.26$	$1^\circ.06$	20.48	20.40	1.00	0.67	0.24	0.02	18.91	17.83	+1.08
5.00 "	$0^\circ.26$	$1^\circ.06$	20.48	20.40	1.00	0.67	0.24	0.02	18.91	17.83	+1.08
8.00 "	$0^\circ.26$	$0^\circ.96$	20.49	20.42	1.01	0.67	0.24	0.02	18.88	17.83	+1.05
11.30 "	$0^\circ.26$	$0^\circ.91$	20.46	20.39	1.01	0.67	0.24	0.02	18.90	17.83	+1.07
Jan. 16											
10.15 A.M.	$0^\circ.26$	$0^\circ.69$	20.47	20.42	1.01	0.67	0.24	0.02	18.88	17.83	+1.05
1.00 P.M.	$0^\circ.26$	$0^\circ.80$	20.48	20.42	1.01	0.67	0.24	0.02	18.88	17.83	+1.05
3.30 "	$0^\circ.26$	$0^\circ.80$	20.47	20.41	1.01	0.67	0.24	0.02	18.89	17.83	+1.06

Displacement of the manometer = 0.34 mm.

Table XXIII.

Original wt. normal concentration of solution, 0.9.
Rotation of original solution, 98°.30 ($t = 21^\circ$).
Rotation at conclusion of exp't, 96°.45 ($t = 21^\circ$).
Loss in rotation, 1°.85 = 1.88 per cent.
Calibration units of air in manometer, 434.93.
Time of setting up cell, 3.30 P. M., Dec. 20, 1906.

Experiment No. 1.
Manometer used, No. 13.
Capillary depression, 0.02.
Cell used, G.
Resistance of membrane, 101,000.
Initial pressure, 20.05 atmospheres.

Time.	Temperature.		Volume of air in manometer.		Corrections.				Osmotic pressure corrected.	Theoretical gas pressure.	Difference between pressure found and calculated.
	Solution.	Air in manometer.	Uncorrected.	Corrected.	Atmospheric pressure.	Liquids in manometer.	Inversion.	Capillary depression.			
Dec. 20											
4.45 P.M.	0°.22	2°.50									
7.30 "	0°.26	0°.94									
Dec. 21											
12.30 A.M.	0°.31	0°.83	19.63	19.57	0.99	0.66	0.29	0.02	21.62	20.06	+1.56
10.00 "	0°.30	0°.84	19.62	19.56	0.99	0.66	0.29	0.02	21.64	20.06	+1.58
12.30 P.M.	0°.32	0°.99	19.63	19.56	0.99	0.66	0.29	0.02	21.64	20.06	+1.58
4.15 "	0°.33	1°.05	19.64	19.56	0.99	0.66	0.29	0.02	21.64	20.06	+1.58

Displacement of the manometer = 0.44 mm.

Table XXIV.

Original wt. normal concentration of solution, 0.9.
Rotation of original solution, 98°.40 (t = 18°.5).
Rotation at conclusion of exp't, 96°.45 (t = 18°.5).
Loss in rotation, 1°.95 = 1.98 per cent.
Calibration units of air in manometer, 434.93.
Time of setting up cell, 3.30 P.M., Dec. 29, 1906.

Experiment No. 2.
Manometer used, No. 13.
Capillary depression, 0.02.
Cell used, G.
Resistance of membrane, 102,000.
Initial pressure, 20.66 atmospheres.

Time.	Temperature.		Volume of air in manometer.		Corrections.				Osmotic pressure corrected.	Theoretical gas pressure.	Difference between pressure found and calculated.
	Solution.	Air in manometer.	Uncorrected.	Corrected.	Atmospheric pressure.	Liquids in manometer.	Inversion.	Capillary depression.			
Dec. 29											
5.30 P.M.	0°.22	1°.80	20.87								
8.00 "	0°.16	1°.06	19.75								
11.30 "	0°.15	0°.97	19.65	19.58	1.01	0.66	0.30	0.02	21.58	20.05	+1.53
Dec. 30											
10.00 A.M.	0°.22	1°.04	19.68	19.61	1.01	0.66	0.30	0.02	21.55	20.05	+1.50
1.00 P.M.	0°.22	1°.13	19.68	19.60	1.00	0.66	0.30	0.02	21.56	20.05	+1.51
5.00 "	0°.25	1°.19	19.69	19.60	1.00	0.66	0.30	0.02	21.56	20.05	+1.51

Displacement of the manometer = 0.05 mm.

Table XXV.

Original wt. normal concentration of solution, 1.0.
Rotation of original solution, 107°.2 (t = 23°).
Rotation at conclusion of exp't, 104°.3 (t = 23°).
Loss in rotation, 2°.9 = 2.71 per cent.
Calibration units of air in manometer, 471.37.
Time of setting up cell, 3.30 P.M., Dec. 12, 1906.

Experiment No. 1.
Manometer used, No. 21.
Capillary depression, 0.02.
Cell used, G.
Resistance of membrane, 90,000.
Initial pressure, 23.00 atmospheres.

Time.	Temperature.		Volume of air in manometer.		Corrections.				Osmotic pressure corrected.	Theoretical gas pressure.	Difference between pressure found and calculated.
	Solution.	Air in manometer.	Uncorrected.	Corrected.	Atmospheric pressure.	Liquids in manometer.	Inversion.	Capillary depression.			
Dec. 12											
5.00 P.M.	0°.14	2°.3									
7.30 "	0°.13	0°.52									
11.10 "	0°.12	0°.44									
Dec. 13											
10.15 A.M.	0°.16	0°.44	18.98	18.95	1.00	0.64	0.46	0.02	24.07	22.28	+1.79
12.30 P.M.	0°.18	0°.59	19.00	18.96	1.00	0.64	0.46	0.02	24.06	22.28	+1.79
4.10 "	0°.18	0°.68	18.99	18.94	1.00	0.64	0.46	0.02	24.09	22.28	+1.81
8.00 "	0°.20	0°.72	19.02	18.97	1.00	0.64	0.46	0.02	24.05	22.28	+1.77
11.15 "	0°.24	0°.75	19.01	18.96	1.00	0.64	0.46	0.02	24.06	22.28	+1.78
Dec. 14											
10.00 A.M.	0°.26	0°.70	19.00	18.95	1.01	0.64	0.46	0.02	24.06	22.29	+1.77
12.30 P.M.	0°.30	0°.72	18.99	18.94	1.01	0.64	0.46	0.02	24.08	22.29	+1.79

Displacement of the manometer = 0.23 mm.

Table XXVI.

Original wt. normal concentration of solution, 1.0.
Rotation of original solution, 107.3 (t = 21°.5).
Rotation at conclusion of exp't, 103°.8 (t = 21°.5).
Loss in rotation, 3°.5 = 3.26 per cent.
Calibration units of air in manometer, 465.78.
Time of setting up cell, 5.30 P. M., Dec. 15, 1906.

Experiment No. 2.
Manometer used, No. 11.
Capillary depression, 0.02.
Cell used, G.
Resistance of membrane, 128,000.
Initial pressure, 24.35 atmospheres.

Time.	Temperature.		Volume of air in manometer.		Corrections.				Osmotic pressure corrected.	Theoretical gas pressure.	Difference between pressure found and calculated.
	Solution.	Air in manometer.	Uncorrected.	Corrected.	Atmospheric pressure.	Liquids in manometer.	Inversion.	Capillary depression.			
Dec. 15											
6.30 P.M.	0°.24	2°.80									
11.30 "	0°.20	1°.00	18.76	18.69	1.00	0.58	0.56	0.02	23.96	22.28	+1.68
Dec. 16											
9.45 A.M.	0°.24	0°.82	18.75	18.69	1.00	0.58	0.56	0.02	23.96	22.28	+1.68
1.00 P.M.	0°.24	0°.83	18.73	18.67	1.00	0.58	0.56	0.02	23.99	22.28	+1.71
6.30 "	0°.24	0°.80	18.73	18.68	1.00	0.58	0.56	0.02	23.97	22.28	+1.69
10.30 "	0°.25	0°.80	18.74	18.68	1.00	0.58	0.56	0.02	23.97	22.28	+1.69
Dec. 17											
10.15 A.M.	0°.25	0°.85	18.73	18.67	1.00	0.58	0.56	0.02	23.99	22.28	+1.71
1.00 P.M.	0°.30	0°.97	18.74	18.67	1.00	0.58	0.56	0.02	23.99	22.29	+1.70
4.00 "	0°.34	0°.96	18.73	18.66	1.00	0.58	0.56	0.02	24.00	22.29	+1.71

Displacement of the manometer = 0.59 mm.

Table XXVII.

Original wt. normal concentration of solution, 1.0.
Rotation of original solution, 107°.2 (t = 20°.5).
Rotation at conclusion of exp't, 105°.2 (t = 20°.5).
Loss in rotation, 2°.0 = 1.87 per cent.
Calibration units of air in manometer, 434.93.
Time of setting up cell, 4.30 P. M., Jan. 14, 1907.

Experiment No. 3.
Manometer used, No. 13.
Capillary depression, 0.02.
Cell used, A.
Resistance of membrane, 134,000.
Initial pressure, 16.13 atmospheres.

Time.	Temperature.		Volume of air in manometer.		Corrections.				Osmotic pressure corrected.	Theoretical gas pressure.	Difference between pressure found and calculated.
	Solution.	Air in manometer.	Uncorrected.	Corrected.	Atmospheric pressure.	Liquids in manometer.	Inversion.	Capillary depression.			
Jan. 14.											
6.00 P.M.	0°.22	2°.60	26.67								
7.30 "	0°.16	1°.19	21.44	21.35							
11.00 "	0°.16	1°.00	19.27	19.20							
Jan. 15											
10.15 A.M.	0°.22	0°.96	17.80	17.74							
1.00 P.M.	0°.26	1°.06	17.80	17.73							
5.00 "	0°.26	1°.06	17.78	17.71							
8.00 "	0°.26	0°.96	17.75	17.69	1.01	0.65	0.31	0.02	23.95	22.29	+1.66
11.30 "	0°.26	0°.91	17.72	17.66	1.01	0.65	0.31	0.02	23.99	22.29	+1.70
Jan. 16											
10.30 A.M.	0°.26	0°.69	17.73	17.69	1.01	0.65	0.31	0.02	23.95	22.29	+1.66
1.00 P.M.	0°.26	0°.80	17.73	17.68	1.01	0.65	0.31	0.02	23.96	22.29	+1.67
3.30 "	0°.26	0°.80	17.73	17.68	1.01	0.65	0.31	0.02	23.96	22.29	+1.67

Displacement of the manometer = 0.91 mm.

Table XXVIII.—*The Osmotic Pressure of Cane Sugar Solutions in the Vicinity of 0°.*

Series III.

Weight normal concentration.	No. of experiment.	Temperature of solution.			Osmotic pressure observed (atmospheres).			Calculated gas pressure for same temperature. Atmospheres.	Difference b'tw'n mean osmotic and mean gas pressure.	Ratio of osmotic to gas pressure.
		Mean.	Highest.	Lowest.	Mean.	Highest.	Lowest.			
0.1	1	0°.26	0°.36	0°.18	2.42	2.42	2.41	2.23	0.19	1.085
"	2	0°.21	0°.26	0°.14	2.44	2.44	2.44	2.23	0.21	1.094
"	3	0°.24	0°.38	0°.14	2.37	2.37	2.36	2.23	0.14	1.063
"	4	0°.24	0°.38	0°.14	2.38	2.39	2.37	2.23	0.15	1.067
0.2	1	0°.22	0°.26	0°.16	4.76	4.77	4.74	4.46	0.30	1.067
"	2	0°.30	0°.32	0°.28	4.75	4.76	4.74	4.46	0.29	1.065
0.3	1	0°.29	0°.34	0°.18	7.02	7.02	7.01	6.69	0.33	1.049
"	2	0°.15	0°.18	0°.14	7.03	7.03	7.02	6.68	0.35	1.052
0.4	1	0°.19	0°.22	0°.16	9.29	9.31	9.27	8.91	0.38	1.043
"	2	0°.28	0°.33	0°.22	9.26	9.26	9.25	8.92	0.34	1.038
"	3	0°.32	0°.34	0°.26	9.30	9.31	9.28	8.92	0.38	1.043
"	4	0°.15	0°.16	0°.12	9.25	9.26	9.25	8.91	0.34	1.038
0.5	1	0°.26	0°.38	0°.14	11.53	11.56	11.52	11.14	0.39	1.035
"	2	0°.23	0°.26	0°.20	11.59	11.61	11.55	11.14	0.45	1.040
"	3	0°.14	0°.18	0°.12	11.65	11.65	11.64	11.14	0.51	1.046
"	4	0°.20	0°.26	0°.16	11.68	11.69	11.67	11.14	0.54	1.048
0.6	1	0°.23	0°.28	0°.16	14.00	14.02	13.98	13.37	0.63	1.047
"	2	0°.21	0°.25	0°.20	13.97	13.98	13.95	13.37	0.60	1.045
0.7	1	0°.26	0°.32	0°.16	16.47	16.48	16.45	15.60	0.87	1.056
"	2	0°.15	0°.16	0°.14	16.55	16.56	16.53	15.60	0.95	1.061
0.8	1	0°.20	0°.26	0°.16	18.93	18.96	18.92	17.82	1.11	1.062
"	2	0°.24	0°.26	0°.16	18.89	18.91	18.88	17.83	1.06	1.059
0.9	1	0°.32	0°.33	0°.30	21.64	21.64	21.62	20.06	1.58	1.079
"	2	0°.21	0°.25	0°.15	21.56	21.58	21.55	20.05	1.51	1.075
1.0	1	0°.22	0°.30	0°.16	24.07	24.09	24.05	22.28	1.79	1.080
"	2	0°.26	0°.34	0°.20	23.98	24.00	23.96	22.28	1.70	1.076
"	3	0°.26	0°.26	0°.26	23.96	23.99	23.95	22.29	1.67	1.075

a dilution of the solution within. The question of dilution and of the distribution, in the correction of results, of loss in rotation between dilution and inversion has been referred to frequently in former papers,[1] and it must continue to be a matter of great concern to us until, through improvements in cells and manipulation, we have succeeded in suppressing dilution or in reducing it to harmless proportions.

Table XXIX.—The Osmotic Pressure of Cane Sugar Solutions in the Vicinity of 0°. Mean Values for Each Concentration.

Series III

Weight-normal concentration.	Temperature.	Observed osmotic pressure. Atmospheres.	Calculated gas pressure. Atmospheres.	Difference between osmotic and gas pressures. Atmospheres.	Ratio of osmotic to gas pressure.
0.1	0°.24	2.40	2.23	0.17	1.077
0.2	0°.26	4.76	4.46	0.30	1.067
0.3	0°.22	7.03	6.69	0.34	1.051
0.4	0°.24	9.28	8.92	0.36	1.040
0.5	0°.21	11.61	11.14	0.47	1.042
0.6	0°.22	13.99	13.37	0.62	1.046
0.7	0°.21	16.51	15.60	0.91	1.058
0.8	0°.22	18.99	17.83	1.08	1.060
0.9	0°.27	21.60	20.06	1.54	1.077
1.0	0°.25	24.00	22.28	1.72	1.077

We have stated[2] that the dilution which occurs in our cells is not due to leakage of the solutions through the membranes. The evidence of this upon which we principally rely at the present time is the demonstrated ability of the membranes to sustain for long periods, undiminished, the maximum pressures which the solutions have, under any circumstances, been found to exert. Solutions in cells with leaky membranes may, and often do, exhibit *constant* pressures for considerable periods, but such pressures are lower than those obtained under the best conditions, and it is characteristic of them that, after some hours, they begin to decline. Sometimes the decline, once begun, is continuous. At other times it is intermittent, each period of decline being followed by one of rising pressure.

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[1] This Journal, **36**, 48, 50; **37** 327.

[2] *Ibid.*, **36**, 32, 43.

Table XXX.—Cane Sugar.

Series III.

Weight-normal concentration.	Number of experiment.	Upward movement of manometer. mm.	Loss in rotation.		Correction for inversion.
			Degrees.	Percentage.	Atmosphere.
0.1	1	0.07	0.20	1.60	0.03
"	2	0.07	0.10	0.80	0.01
"	3	0.09	0.05	0.39	0.01
"	4	0.09	0.10	0.79	0.01
0.2	1	0.05	0.15	0.61	0.02
"	2	0.05	0.15	0.60	0.02
0.3	1	0.06	0.50	1.37	0.07
"	2	0.06	0.60	1.64	0.08
0.4	1	0.08	0.55	1.15	0.08
"	2	0.07	0.60	1.25	0.08
"	3	0.22	0.40	0.83	0.06
"	4	0.04	0.40	0.83	0.06
0.5	1	0.24	0.90	1.53	0.13
"	2	0.22	1.00	1.70	0.14
"	3	0.07	1.05	1.71	0.15
"	4	0.38	0.75	1.29	0.11
0.6	1	0.48	1.20	1.73	0.12
"	2	0.10	1.30	1.86	0.14
0.7	1	0.61	1.20	1.51	0.18
"	2	0.45	1.10	1.39	0.16
0.8	1	0.01	1.55	1.74	0.23
"	2	0.34	1.60	1.80	0.24
0.9	1	0.44	1.85	1.88	0.29
"	2	0.05	1.95	1.98	0.30
1.0	1	0.23	2.90	2.71	0.46
"	2	0.59	3.50	3.26	0.56
"	3	0.91	2.00	1.87	0.31
(1)	(2)	(3)	(4)	(5)	(6)

Such conduct on the part of leaky cells is not difficult to explain. There is, apparently, in these cases a period, more or less prolonged, during which the intake of water through the membrane is in equilibrium with the escape of solution from the cell, and the pressure therefore remains constant. As soon, however, as the solution becomes diluted to such an extent that it can, on further dilution, no longer maintain the pressure, a fall of the mercury in the manometer sets in, which may be, and often is, interrupted by a subsequent rise due to the repair of the membrane by the membrane-forming salts

Table XXXI.—Cane Sugar.

Series III.

			Osmotic pressure.		
Weight-normal concentration.	No. of experiment.	Calculated gas pressure.	1. If all loss in rotation is ascribed to invers'n.	2. If all loss in rotation is ascribed to dilution.	3. If half the loss in rotation is ascribed to dilution.
0.1	1	2.23	2.42	2.51	2.48
“	2	2.23	2.44	2.48	2.46
“	3	2.23	2.37	2.39	2.39
“	4	2.23	2.38	2.42	2.41
0.2	1	4.46	4.76	4.83	4.80
“	2	4.46	4.75	4.81	4.79
0.3	1	6.69	7.02	7.20	7.14
“	2	6.68	7.03	7.25	7.18
0.4	1	8.91	9.29	9.49	9.43
“	2	8.92	9.26	9.47	9.40
“	3	8.92	9.30	9.45	9.41
“	4	8.91	9.25	9.40	9.35
0.5	1	11.14	11.53	11.84	11.75
“	2	11.14	11.59	11.96	11.85
“	3	11.14	11.65	12.03	11.91
“	4	11.14	11.68	11.96	11.87
0.6	1	13.37	14.00	14.39	14.25
“	2	13.37	13.97	14.40	14.25
0.7	1	15.60	16.47	16.92	16.78
“	2	15.60	16.55	16.97	16.83
0.8	1	17.82	18.93	19.52	19.34
“	2	17.83	18.89	19.51	19.32
0.9	1	20.06	21.64	22.37	22.15
“	2	20.05	21.56	22.33	22.10
1.0	1	22.28	24.07	25.23	24.87
“	2	22.28	23.98	25.41	24.98
“	3	22.29	23.96	24.74	24.50
(1)	(2)	(3)	(4)	(5)	(6)

which are always present. The mercury, however, in such cases never quite reaches the point from which the previous decline set in. It may, nevertheless, after having reached its highest point, remain stationary for a considerable time, showing that the intake of water and the escape of solution are again temporarily in equilibrium.

Formerly we did not rely upon the ability of the membranes to develop continuously the maximum pressures, and to sustain them for long periods, as the only test of the soundness of the membranes. We also carefully examined the liquid in which the cell is immersed during an experiment for evidences of the presence of the substance whose pressure had been measured. The result was to convince us that the conduct of the cell in the bath may be relied upon to reveal any defects of the membrane or of cell construction.

Table XXXII.—Cane Sugar. Mean Value for Each Concentration.

Series III.

			Osmotic pressure.		
Weight-normal concentration.	Temperature.	Calculated gas pressure.	1. If all loss in rotation is ascribed to invers'n.	2. If all loss in rotation is ascribed to dilution.	3. If half the loss in rotation is ascribed to dilut'n.
0.1	0°.24	2.23	2.40	2.45	2.44
0.2	0°.26	4.46	4.76	4.82	4.80
0.3	0°.22	6.69	7.03	7.23	7.16
0.4	0°.24	8.92	9.28	9.45	9.40
0.5	0°.21	11.14	11.61	11.95	11.85
0.6	0°.22	13.37	13.99	14.40	14.25
0.7	0°.21	15.60	16.51	16.95	16.81
0.8	0°.22	17.83	18.99	19.52	19.33
0.9	0°.27	20.06	21.60	22.35	22.13
1.0	0°.25	22.28	24.00	25.13	24.78
(1)	(2)	(3)	(4)	(5)	(6)

If our membranes did not leak, the dilution of the cell contents was due, in the main, to the causes so frequently mentioned in former papers,[1] namely: 1. The slipping of the manometer in the stopper, or the crowding upwards of both manometer and stopper when the former could not slip in the latter; 2. The sucking in of water from the wall while the cell was being closed for a measurement, and again while it was being taken apart after an experiment.

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[1] This Journal, **36**, 24, 26, 48; **37**, 327.

The first of these difficulties, *i. e.*, dilution due to displacements of manometers and stoppers, has been overcome through improvements in method and manipulation. To what extent the remedy has been effective is shown in Table XXX.,

Table XXXIII.—Cane Sugar.

Series III.

			Ratio of osmotic to gas pressure.		
Weight-normal concentration.	No. of experiment.	Calculated gas pressure.	1. If all loss in rotation is ascribed to inversion.	2. If all loss in rotation is ascribed to dilution.	3. If half the loss in rotation is ascribed to dilut'n.
0.1	1	2.23	1.085	1.126	1.112
"	2	2.23	1.094	1.112	1.103
"	3	2.23	1.063	1.072	1.072
"	4	2.23	1.067	1.085	1.081
0.2	1	4.46	1.067	1.083	1.076
"	2	4.46	1.065	1.078	1.074
0.3	1	6.69	1.049	1.076	1.067
"	2	6.68	1.052	1.085	1.075
0.4	1	8.91	1.043	1.065	1.058
"	2	8.92	1.038	1.062	1.054
"	3	8.92	1.043	1.059	1.055
"	4	8.91	1.038	1.055	1.049
0.5	1	11.14	1.035	1.063	1.055
"	2	11.14	1.040	1.074	1.064
"	3	11.14	1.046	1.080	1.069
"	4	11.14	1.048	1.074	1.066
0.6	1	13.37	1.047	1.076	1.066
"	2	13.37	1.045	1.077	1.066
0.7	1	15.60	1.056	1.085	1.076
"	2	15.60	1.061	1.088	1.079
0.8	1	17.82	1.062	1.095	1.085
"	2	17.83	1.059	1.094	1.084
0.9	1	20.06	1.079	1.115	1.104
"	2	20.05	1.075	1.114	1.102
1.0	1	22.28	1.080	1.132	1.116
"	2	22.28	1.076	1.140	1.121
"	3	22.29	1.075	1.110	1.099
(1)	(2)	(3)	(4)	(5)	(6)

column 3, in which are recorded the total upward movements of the manometers in the present series of experiments. It will there be seen that the displacement was in no case sufficient sensibly to affect the concentration of the cell contents.

Unfortunately, however, the measures which were taken to secure the manometers and stoppers more firmly in their places have prolonged somewhat the time within which a cell can be closed and opened, so that dilution due to the second cause mentioned above is probably a little greater now than formerly.

Table XXXIV.—Cane Sugar. Mean Values for Each Concentration.

Series III.

			Ratio of osmotic to gas pressure.		
Weight-normal concentration.	Temperature.	Calculated gas pressure.	1. If all loss in rotation is ascribed to invers'n.	2. If all loss in rotation is ascribed to dilution.	3. If half the loss in rotation is ascribed to dilution.
0.1	0°.24	2.23	1.077	1.099	1.092
0.2	0°.26	4.46	1.067	1.081	1.075
0.3	0°.22	6.69	1.051	1.081	1.071
0.4	0°.24	8.92	1.040	1.060	1.054
0.5	0°.21	11.14	1.042	1.073	1.064
0.6	0°.22	13.37	1.046	1.077	1.066
0.7	0°.21	15.60	1.058	1.087	1.078
0.8	0°.22	17.83	1.060	1.095	1.085
0.9	0°.27	20.06	1.077	1.115	1.103
1.0	0°.25	22.28	1.077	1.127	1.112
(1)	(2)	(3)	(4)	(5)	(6)

The losses of rotation which the solutions suffered while in the cells are all brought together in Table XXX., where they are stated in the form of saccharimeter degrees (column 4) and in that of percentages of original rotation (column 5). These values, in our judgment, are the extreme measure of the uncertainty of our determinations of osmotic pressure. The loss in rotation is due partly to inversion and partly to dilution, and it is impossible to ascertain with any satisfactory degree of certainty how much of it is to be ascribed to either of the two causes. The correction for inversion,[1] when applied to the observed pressure, lowers it, while that for dilution raises it; that is, the two corrections are of a compensating character.

In column 6 of Table XXX. are given, in fractions of an atmosphere, the corrections for each experiment if all the observed loss in rotation is ascribed to inversion and no allowance is made for dilution. These are the quantities which have been subtracted from the observed pressures as corrections in all the tables from I. to XXX. The results are unquestionably somewhat too low because a part of the loss of rotation, all of which has hitherto been ascribed to inversion, was due to dilution, the correction for which, if it could be applied, would be added to the observed pressures.

In order to show the effect of corrections for dilution, Tables XXXI. and XXXII. have been added. The former gives the results of the individual experiments as they would stand:

1. If all loss of rotation is ascribed to inversion and no correction is made for dilution (column 4).

2. If all loss in rotation is ascribed to dilution and no correction is made for inversion (column 5).

3. If one-half the observed loss in rotation is ascribed to dilution and no account is taken of inversion.

In Table XXXII. the same data are presented in condensed form as mean values for each concentration.

Just as the results given in column 4 (Tables XXXI. and XXXII.) are too low because no account is taken of *dilution*, so are those in column 5 too high, because no correction for *inversion* has been made. In the earlier work[2] it was attempted to determine by the method of Fehling the amount of the inversion which takes place in the cell, and the attempt has since been repeated, but without convincing results. It may be stated, however, that, though evidences of inversion are never wanting when the test is applied to a solution, after its removal from the cell, the largest amount which appeared to be found by the method of Fehling has not exceeded, even in weight-normal solutions, the quantity which, as a correction for observed pressures, would be equivalent to 0.05 atmosphere. In other words, if the indications obtained by the Fehling method are even approximately quantitative, the values recorded in column 6 of Table XXX., as corrections, are considerably too large, and the pressures given in column 4 in Tables XXXI. and XXXII. are accordingly, to an equal degree, too low.

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[1] THIS JOURNAL, 36, 41.

[2] *Ibid.*, 34, 30.

The reason for introducing column 6 (Tables XXXI. and XXXII.) requires explanation. In this are presented the pressures for the various weight-normal concentrations of solution as they would stand if the observed pressures were corrected for one-half the loss of rotation, without any correction for inversion. In our judgment, the values in column 6 are still somewhat too high. The basis for this opinion will be found in the following explanation: The time now required to close a cell—*i. e.*, the time elapsing between the filling in of the solution and the screwing down of the manometer nut—varies from 8 to 15 minutes, and the time usually spent in opening the cell at the close of an experiment—*i. e.*, the time from the loosening of the manometer nut to that of emptying the cell—is about the same, that is, it varies from 8 to 15 minutes. Whatever dilution of the cell contents occurs during the closing of the cell affects the observed pressure, while that which occurs during the opening of it does not. Hence, before correcting the observed pressures for loss in rotation, that portion of it which is due to dilution occurring during the opening of the cell should be deducted. We have no means, however, of ascertaining what proportion of the whole dilution, as measured by loss of rotation, is to be thus deducted. But it is safe to assume that more than half of the dilution occurs subsequent to the measurement of pressure; for, during the period in which the cell is being closed, the contents are all the time under increased pressure, while during the time in which it is being opened, they are as constantly under strongly diminished pressure. We have, therefore, ventured to deduct one-half of the observed loss of rotation before correcting the observed pressures for dilution and to present the results in column 6 of Tables XXXI. and XXXII. We also venture to predict that, when we remeasure the osmotic pressure of cane sugar solutions in the vicinity of 0°, after having so improved our cells as nearly to suppress dilution, we shall find pressures for the various concentrations which lie between those recorded in columns 4 and 6 of Tables XXXI. and XXXII. In other words, we judge that the measurements as presented in column 4 of the tables are still uncertain only within the limits indicated below:

Weight-normal concentration.	Limit of uncertainty.	
	Atmosphere.	Percentage.
0.1	0.04	1.66
0.2	0.04	0.84
0.3	0.13	1.85
0.4	0.12	1.29
0.5	0.24	2.07
0.6	0.26	1.86
0.7	0.30	1.82
0.8	0.34	1.79
0.9	0.53	2.45
1.0	0.78	3.25

It is obvious that if the assumption that more dilution occurs while the cells are being opened than while they are being closed is correct, later work under better conditions can only tend to diminish the magnitude of the now uncertain values recorded above, for any correction whatever for inversion will diminish the values given in column 6 of Tables XXXI. and XXXII., while any correction of previously underestimated dilution occurring during the process of opening the cell will raise the values in column 4.

We have endeavored in two ways to secure some safe basis for judgment in respect to the matters discussed above. In the first place, in order to ascertain whether a considerable proportion of the loss in rotation is due, as was suspected, to dilution rather than to inversion, the cells, just before they were closed, and again just before they were opened, were dipped, in many instances, in a solution of sugar whose concentration was the same as that of the solution under investigation. In all such cases, the loss of rotation was much less than —often less than half—that of solutions in cells which had not been so treated, provided no unusually long time was consumed in the closing and opening processes. It is hardly necessary to state that cells which had been dipped were carefully cleansed externally before placing them in the bath. The practice of dipping has proved so efficacious as a means of reducing loss of rotation that it is now employed with all cells.

Again, in order to discover, if possible, whether more dilution occurs while opening than while closing the cells, a record of the time consumed in each performance has been kept, and this shows that the loss in rotation is affected more by any unusual prolongation or shortening of the time employed in the former than in the latter operation.

The most important fact which has been brought out by this series of measurements is that the osmotic pressure of cane sugar solutions, in the vicinity of the freezing point of the solvent, considerably exceeds the calculated gas pressures for the same temperatures. Tables XXXIII. and XXXIV. have been introduced in order to facilitate a comparison of the two sets of values. In them the ratios of osmotic to gas pressures are given in three ways (columns 4, 5, and 6), according to each of the possible methods of correcting the observed pressures for the loss in rotation which occurs in the cell. The fact of an excess of osmotic over gas pressure at low temperatures appears to be established whatever may be the view which is accepted as to the proper method of correcting the observed pressures for loss in rotation.

Any attempt to explain the apparently abnormal(?) pressures of cane sugar solutions in the vicinity of 0° would be premature at the present time, and any discussion of the question must continue to be unprofitable until a much larger number of pertinent facts have been firmly established by experiment. Some may see in the high pressures which have been obtained an evidence of the hydration of cane sugar in solution, and may point to the abnormal(?) freezing points of such solutions as a confirmation of the correctness of this view. But, as we shall show in our next communication, the osmotic pressures of glucose solutions in the vicinity of 0° also exceed the calculated gas pressures for the same temperatures, and this despite the fact that whatever evidence can be secured from the freezing points is to the effect that glucose in solution is not hydrated.[1]

Others may discover in the high pressures in question, and in the fact that they are, in a general way, nearly equal to those which were obtained in the vicinity of 20°, a suggestion that osmotic pressure, unlike that of gases, *has little or no temperature coefficient.* But an equally just suspicion, apparently, is that somewhere between 0° and 20° a temperature may be found at which osmotic pressure, like the volume of the solvent, is at a *minimum*, and from which it increases, with change of temperature, in both directions. Our methods are probably already sufficiently accurate to enable us to determine with certainty whether such a minimum exists, and we have, accordingly, begun a series of measurements at temperatures between 0° and 20°.

Attention is called to a peculiarity of the ratios in columns 4, 5, and 6 of Table XXXIV. It will there be seen that the ratio of osmotic to gas pressure in case of cane sugar appears to reach a minimum with the 0.4 weight-normal solution. It was the appearance of this relation which induced us to make a larger than usual number of measurements of the pressures of the 0.1, 0.4, and 0.5 normal solutions (see Table XXXIII.). We do not, however, regard the reality of this apparent minimum ratio as established. It was stated in a former paper[2] that some uncertainty exists as to the exact osmotic equivalence of the small quantities of membrane-forming salts which are employed in connection with the measurements of pressure; that, if the evidence of the freezing points is reliable, the ferrocyanide is dissociated into 8 instead of 5 ions. If this is true, the osmotic pressure of the ferrocyanide within the cell is probably slightly greater than that of the copper sulphate in the water in which the cell is immersed, and a slight correction should be made for the inequality. The correction, if one is to be made, is small, owing to the smallness of the quantities of the membrane-forming salts which are used, but it may be of sufficient magnitude to affect sensibly the ratio in question in the case of the most dilute solutions. Its effect upon the ratios would, of course, be inversely proportional to the concentration of the solutions. We have delayed attacking, except in a superficial way, the problem of a possible slight osmotic inequality of our membrane-forming salts until we could complete the preparations, now in progress, for the simultaneous determination of the osmotic pressure and of the dissociation of electrolytes.

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[1] THIS JOURNAL, 37, 360.

[2] *Ibid.*, 36, 33.

Johns Hopkins University,
February 1, 1907.

ON SOME CUPRAMMONIUM SALTS. III.[1]

By David W. Horn.

The object of this paper is to present further evidence of the correctness of the point of view presented in the previous communication.[2]

Cuprammonium salts are known that correspond to each of the following formulae:

$$\begin{gathered}Cu(Ac')_2.NH_3;\\ Cu(Ac')_2.2NH_3;\\ Cu(Ac')_2.4NH_3;\\ Cu(Ac')_2.5NH_3;\\ Cu(Ac')_2.6NH_3.\end{gathered}$$

That the number of salts represented by some of these formulae is small may be attributed to the limited knowledge of this group of compounds.

When this study of cuprammonium salts began, there was no general theory that accounted satisfactorily for all these various types. The idea expressed in text-books and elsewhere that cuprammonium salts conform to 2 types,

$$Cu(NH_3)_2(Ac')_2 \quad \text{and} \quad Cu(NH_3)_4(Ac')_2,$$

has not only proved unproductive, but also misleading. There have never been data available to suggest the way in which Werner's conceptions, in their original form, could be used to account for salts of the general formulae,

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[1] Read in abstract before the Philadelphia Section, American Chemical Society, Oct. 18, 1906.

[2] This Journal, 35, 271 (1906).

$$Cu(Ac')_2.NH_3 \quad \text{and} \quad Cu(Ac')_2.5NH_3.$$[1]

The recent attempt made by Pfeiffer[2] to modify Werner's conceptions so as to include all cuprammonium salts rests upon so many assumptions that its value may be seriously questioned. However, without some general conception of these compounds it is difficult to see how any considerable advance in knowledge of them could be made.

As stated in the preceding paper, in the work that has been in progress in this laboratory for some time, cuprammonium salts are studied with reference to the equilibria in the systems in which the salts form. It was there shown that this point of view has distinct advantages over previous ones in that cuprammonium salts formed from anhydrous copper salts and dry ammonia gas are included logically in the same class as those formed in solutions, and in that all necessity for regarding cuprammonium salts of any degree of complexity as abnormal or unusual is thus removed.

From this point of view, at any one temperature, the complexity of a cuprammonium compound is dependent partly upon the concentrations of ammonia, copper salt and water in the system where it forms, and partly upon the nature of the acid residue. It has been shown previously how the data then available suggested this view as a probable one.

The experiments in the present paper show more definitely than was possible before, the dependence of the complexity of a cuprammonium compound upon the concentration of ammonia, copper salt and water in the system where it forms. More definite treatment of the specific effect of the acid residue will be given in a later paper.

Prior to the appearance of my previous paper, Kohlschütter[3] had given additional weight to the idea that there are *two* types to which cuprammonium compounds conform, an idea that has always had a retarding influence on the development of knowledge of these compounds. Consequently, I then called attention to Kohlschütter's work and presented the cuprammonium oxalates as prima facie evidence against the two-type idea and as directly suggestive of the point of view that I then discussed. Kohlschütter has since[1] adopted the suggestion, in a limited way, in his recent study of thiocarbamid compounds of cuprous salts, and has proposed the name "Atomaffitat" to account for the effect of the acid residue. This indefinite term seems to add little, if anything, but obscurity to a subject already obscure because of the small amount of data available.

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[1] Z. anorg. Chem., 3, 303 (1893).

[2] *Ibid.*, 48, 98 (1905).

[3] Ber. d. chem. Ges., 37, 1153 (1904).

From the point of view of the equilibrium involved, there should be for each temperature a series of definite ratios,

$$x \text{ mols. } NH_3 : y \text{ mols. } Cu\,(Ac')_2 : z \text{ mols. } H_2O,$$

which would permit the formation of a cuprammonium salt of one degree of complexity and exclude the possibility of formation of a salt of any other degree of complexity. As the values of x, y and z change, the ratio should approach limits beyond which the favored salt could no longer form, but in its place a more or less complex salt would appear.

The simplest case for the experimental test of this reasoning would consist of 2 cuprammonium salts, both of which could be obtained from aqueous solutions without "water of crystallization." As fulfilling these conditions, the salts

$$Cu(SCN)_2.2NH_3 \quad \text{and} \quad Cu(SCN)_2.4NH_3$$

were selected.

Some discussion of the preparation and properties of these salts appears later in this paper, along with analyses that serve for identification.

To determine the unknown values in the ratio

$$x \text{ mols. } NH_3 : y \text{ mols. } Cu(Ac')_2 : z \text{ mols. } H_2O,$$

corresponding to the stability of each salt, the solid salts, freshly prepared, were shaken, at constant temperature, with ammonia water of different concentrations until the concentrations of ammonia and copper salt in the resulting solutions became constant. Weighed quantities of the saturated solutions were then analyzed for ammonia and thiocyanion and water was calculated by difference.

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[1] Ann. Chem. (Liebig), **349**, 252 *et seq.* (1906).

The results obtained in this way, at 25°, appear in the table on the opposite page.

When the figures (in the last two columns) corresponding to the values of x' and y' in the ratio

$$x' \text{ mol. } NH_3 : y' \text{ mol. } Cu(SCN)_2 : 1000 \text{ mol. } H_2O,$$

are plotted to show the interdependence of the concentrations of ammonia and copper salt at constant concentration of water, the solubility curve shown in the following figure, I., is obtained:

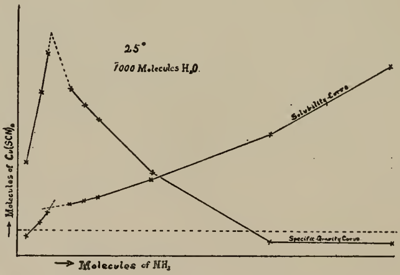

Fig. I.

The 2 parts of this solubility curve show clearly that the interdependence referred to is quite different for the 2 different salts in contact with their saturated solutions. The 2 parts of the curve prove the existence of 2 distinct series of definite ratios,

$$x \text{ mols. } NH_3 : y \text{ mol. } Cu(SCN)_2 : z \text{ mols. } H_2O,$$

any ratio of each series representing conditions under which 1, and only 1, of the 2 cuprammonium salts can exist, in stable equilibrium, at the given temperature. Any ratio of each

Table I.—Solubility of Copper Sulphocyanate in Ammonia Water at 25°.

No. of solution.	One gram of solution contains			One hundred molecules of the mixture contain			One thousand molecules of water dissolve		Composition of solid salt in contact with solution.
	gram NH_3.	gram $Cu(SCN)_2$.	gram H_2O.	x mols. NH_3.	y mols. $Cu(SCN)_2$.	z mols. H_2O.	x' mols. NH_3.	y' mols. $Cu(SCN)_2$.	
1	0.2147	0.1522	0.6331	25.90	1.74	72.34	358.04	24.09	$Cu(SCN)_2.4NH_3$
2	0.1655	0.1124	0.7221	19.24	1.24	79.50	242.02	15.60	
3	0.0993	0.0798	0.8209	11.23	0.86	87.92	127.76	9.74	
4	0.0639	0.0659	0.8702	7.14	0.70	92.15	77.51	7.59	
5	0.0535	0.0622	0.8843	5.98	0.66	93.36	64.05	7.04	
6	0.0426	0.0596	0.8978	4.75	0.63	94.63	50.21	6.65	
7	0.0250	0.0511	0.9239	2.76	0.54	96.72	28.55	5.55	$Cu(SCN)_2.2NH_3$
8	0.0198	0.0408	0.9394	2.17	0.42	97.41	22.27	4.35	
9	0.0079	0.0245	0.9676	0.85	0.25	98.89	18.61	2.54	

series then favors but one degree of complexity in cuprammonium sulphocyanates and excludes the possibility of stable existence of the cuprammonium sulphocyanate of the other degree of complexity. There is one ratio of which this is not true; it is the ratio common to both series and is the only ratio representing conditions under which both cuprammonium salts can exist side by side. This may be called the "transition ratio" for the 2 salts. It is represented by the "break" in the solubility curve.

As a check upon the probable existence of this unique condition in the saturated solution, corresponding to the transition ratio, the specific gravities of the saturated solutions were determined. The values obtained appear in the following table, II., in which the numbers in column 1 refer to the same solutions as the numbers in column 1, Table I.:

Table II.—Specific Gravities of Saturated Solutions at 25°.

Number of solution.	Molecules NH_3 present for every 1000 mols. H_2O.	Sp. gr. at 25° referred to water at 25°.	Sp. gr. minus 1.	1000 × (sp. gr. —1).
1	358.04	0.99853	0.00147	—1.5
2	242.02	0.99871	0.00129	—1.3
3	127.76	1.00703	0.00703	7.0
4	77.51	1.01336	0.01336	13.4
5	64.05	1.01506	0.01506	15.1
6	50.21	1.01705	0.01705	17.1
7	28.55	1.02132	0.02132	21.3
8	22.27	1.01661	0.01661	16.6
9	8.61	1.00816	0.00816	8.2

In Fig. I., the curve marked "specific gravity curve" represents the interdependence of the specific gravity and the concentration of ammonia in the ratios mentioned above. For purposes of graphic representation the values actually plotted are not the specific gravities but the specific gravities *minus* 1. The dotted axis in the figure is the axis of abscissae for the specific gravity curve; the axis of ordinates coincides with the corresponding axis for the solubility curve.

It is evident that the saturated solution represented by "the transition ratio" is unique in occupying a *minimum* volume, and that the existence of the 2 distinct series of ratios shown by the solubility curve is confirmed by the specific gravity curve.

It was pointed out in the previous paper that one necessary condition in considering cuprammonium salts from the point of view suggested is that the temperature shall be the same in all cases. There was sufficient reason for believing that the extent and character of the series of ratios corresponding to any one salt would vary with the temperature. In the following table, III., are given the results of the analyses of saturated solutions prepared at 40°.

In Fig. II. these results are plotted just as the results at 25° were plotted in Fig. I. A comparison of the 2 solubility curves shows definitely the variations of the 2 series of ratios and of the transition ratio with the temperature.

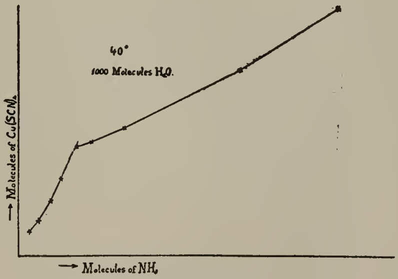

Fig. II.

This study of the sulphocyanates was made to test the correctness of the point of view we had adopted, and can be regarded only as of a preliminary character. It is safe to predict, however, that the results will all be of the same general character when suitable salts are at hand and the work is extended to include cuprammonium salts of the various hydrated and anhydrous types.

Table III.—Solubility of Copper Sulphocyanate in Ammonia Water at 40°.

Number of solution.	One gram of solution contains			One hundred molecules of the mixture contain			One thousand molecules of water dissolve		Composition of solid salt in contact with solution.
	gram NH_3.	gram $Cu(SCN)_2$.	gram H_2O.	x mols. NH_3.	y mols. $Cu(SCN)_2$.	z mols. H_2O.	x' mols. NH_3.	y' mols. $Cu(SCN)_2$.	
10	0.1802	0.1976	0.6222	22.89	2.38	74.73	306.28	31.83	$Cu(SCN)_2.4NH_3$
11	0.1398	0.1658	0.6944	17.23	1.93	80.84	213.10	23.93	
12	0.0758	0.1299	0.7943	9.04	1.47	89.49	101.00	16.38	
13	0.0550	0.1207	0.8243	6.50	1.35	92.15	70.59	14.67	
14	0.0435	0.1178	0.8388	5.13	1.32	93.56	54.82	14.07	
15	0.0352	0.0876	0.8772	4.04	0.95	95.01	42.53	10.00	$Cu(SCN_2).2NH_3$
16	0.0257	0.0655	0.9088	2.89	0.70	96.41	30.00	7.22	
17	0.0177	0.0418	0.9405	1.94	0.44	97.63	19.86	4.46	
18	0.0094	0.0281	0.9625	1.02	0.29	98.69	10.31	2.93	

This prediction is made upon the basis of the Phase Rule. In all cases like this one the systems studied will be of the third order, with ammonia, copper salt and water as the components. In systems where a cuprammonium salt of but one degree of complexity can form there will be 3 phases: 1 solid, the cuprammonium salt; 1 liquid, the saturated solution; and 1 vapor phase, a mixture of ammonia and water vapor. All such systems will be divariant like the 2 series of systems we have studied.

In such divariant systems the state of the system is perfectly defined when 2 of the 3 factors, pressure, temperature, or concentration, of the components in the liquid phase are arbitrarily fixed. The concentration of the components in the vapor phase is dependent directly upon their concentration in the liquid, and the concentration of the components in the solid phase is fixed by the law of definite proportions. In our study of the sulphocyanates we have fixed arbitrarily the temperature and the concentration of ammonia and water, 2 out of the 3 interdependent concentrations, in the liquid phase. In such divariant systems, according to the Phase Rule, there must be, for every arbitrarily selected temperature, a series of concentration ratios of the components in the liquid phase, corresponding to stable equilibrium in the system, and for every arbitrarily selected concentration ratio, a series of temperatures. The existence of the series of ratios for each temperature has already been shown for each of the sulphocyanates, and the existence of a series of temperatures for each ratio will be shown in Fig. III.

When a new salt appears in such a system, the system becomes monovariant, and for each arbitrarily selected temperature there can be but *one* concentration ratio of the components in the liquid phase that will satisfy conditions for stable equilibrium, *i. e.*, "the transition ratio."

As a special case under the Phase Rule, the comparatively limited data presented in this paper may be generalized graphically[1] to show more clearly the interdependence of temperature, concentration ratio and complexity of cuprammonium salt.

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[1] Compare Roozeboom and Schreinemakers: Z. physik. Chem., **15**, 595 (1894). "Gleichgewichte in System: Wasser, Chlorwasserstoff, Eisenchlorid."

In Fig. III., the XT-plane is the plane of zero concentration of copper salt; the YT-plane, the plane of zero concentration of ammonia; and the T-line in which the 2 planes intersect at right angles to each other is the temperature axis along which rising temperature is measured in the direction of the arrow, the XY-plane being parallel to the plane of zero temperature. The figure is drawn to scale. Within the limits of concentration and temperature observed in the experiments, the 2 surfaces represent all conditions of concentration and temperature under which the 2 sulphocyanates can exist in contact with their solutions in aqueous ammonia. The line PP′ is the path of the transition ratio as temperature changes.

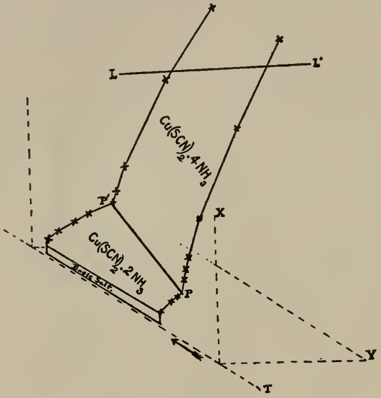

Fig. III.

By the aid of the figure it is possible to indicate, with a fair degree of probability, certain things that would be found to be true beyond the limits of the experiments. The true outer limit of the surface for the salt $Cu(SCN)_2.4NH_3$ must remain unknown, for it is possible, experimentally, to get only a limited amount of ammonia into any aqueous solution at a fixed temperature. The more elevated the temperature for any known aqueous solution, the less ammonia can be dissolved. The limit actually imposed on the surface for the salt,

$$Cu(SCN)_2.4NH_3,$$

then, must, at constant concentration of copper salt, incline, with rising temperature, toward the YT-plane, let us say parallel to LL′, so that the surface must grow narrower as the temperature rises. It is evident from the figure that the surface for the salt $Cu(SCN)_2.2NH_3$ grows broader with rising temperature. If both salts continue in existence as the temperature rises, a temperature is indicated by the figure where the surface for the more complex salt will have diminished to a point, and beyond which only the less complex salt can exist. Conversely, a low temperature is indicated by the figure, beyond which it would be impossible to prepare the less complex salt from aqueous solution.

The one limit of the surface for the salt $Cu(SCN)_2.2NH_3$ is the line PP′, the path of the transition ratio. The other limit corresponds to the appearance of a basic salt. The salt $Cu(SCN)_2.2NH_3$ is *insoluble* in water, but soluble in water that contains a small amount of ammonia. If a solution of the salt in dilute ammonia water is diluted with water a basic salt of pale blue-green color is precipitated when a certain definite dilution is reached. This precipitate always forms at the same dilution, at constant temperature, as we have found in analogous experiments with cuprammonium sulphate. There must be, then, for each temperature, a transition ratio for the basic salt and the salt $Cu(SCN)_2.2NH_3$, and with rising temperature there must be a change in this transition ratio, the path of which, represented graphically, will be the other limit to the surface for the salt $Cu(SCN)_2.2NH_3$. For a fixed concentration of ammonia and of water the decomposition into basic salt (hydrolysis) will be greater the higher the temperature, so that it is probable that the limit of the surfaces for $Cu(SCN)_2.2NH_3$ and the basic salt inclines toward the XT-plane and accentuates the broadening of this plane with rising temperature and its narrowing with falling temperature.

This limit lies near the values realized in the experiments in the most dilute solutions.

Considering some of the changes possible in any concentration ratio,

$$x \text{ mol. } NH_3 : y \text{ mol. } Cu(SCN)_2 : z \text{ mol. } H_2O,$$

it is clear that x, y, or z might diminish until it approached to or equaled zero. When $z = 0$ we have for study the formation of cuprammonium sulphocyanates from anhydrous copper sulphocyanate and dry ammonia. So that, in general, the formation of cuprammonium salts from anhydrous copper salt and dry ammonia is only a special case, the limiting case, of the formation of all of the ammonia compounds, hydrated and anhydrous, of the given copper salt.[1]

This direct relation could have been shown graphically if we had plotted the values in columns 5, 6 and 7, Tables I. and III., in the triangular diagram[2] that is frequently used for isotherms in ternary systems, but the numerical values of y, the mols. of copper sulphocyanate, are so small that the graphs are less satisfactory than Figs. I. and II., and their combination, than Fig. III. The relation in the general case is readily seen from Fig. IV., where the pure components are represented at the angles of a triangular right prism,[3] within which all concentration ratios of the 3 components may be plotted at temperatures measured along the perpendicular axis of the

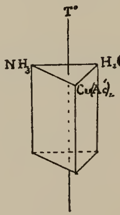

Fig. IV.

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[1] Cf. THIS JOURNAL, 35, 284 (1906).

[2] Gibbs: T. Conn. Acad., 3, 176 (1876).

[3] *Vide* Ostwald: Lehrb. d. Alge. Chem., II, 2, 982 *et seq.*

prism. One of the lateral faces, it will be seen, is a part of the diagram that would represent the formation of cuprammonium salts from anhydrous copper salt and dry ammonia; another, a part of the diagram that would represent the formation of hydrated copper salts from anhydrous copper salt and water. Of course, the partial character of these planes, as compared with the diagrams of which they are a part, is due to the fact that they represent systems only at one pressure, the average pressure of solubility determinations, about 1 atmosphere. The influence of pressure cannot be neglected in the formation of hydrates and of cuprammonium salts in the absence of water, as it may be in solubility work, where its effect is so small. I have already made some progress in the study of systems consisting of anhydrous copper salt and dry ammonia, but am not ready to discuss the experiments.

Further consideration of the effect of the acid residue will show that the ideas advanced represent a special case in the general problem of complex compounds. The nature of the metal, the acid residue, or the addendum, may vary, while the 2 remaining factors in the complex molecule are unchanged. In cuprammonium salts the metal and the addendum remain the same while the acid residue varies; consequently, when the temperature is fixed, the specific effect of the acid residue is the other influence, besides concentration, that affects the complexity. In a comparison of the properties of the complex compounds of any one copper salt with different addenda, as ammonia, pyridine, ethylenediamine, water, etc., the specific effect of the addendum takes the place of that of the acid residue. When a comparison between cuprammonium chloride, cadmium ammonium chloride, zinc ammonium chloride, nickel ammonium chloride, etc., is made, the specific effect of the metallic atom takes the place of that of the acid residue.

The case of cuprammonium salts is less simple than some others because the compounds frequently form in aqueous solution, where the solvent decomposes the compound to an extent proportional to the relative concentration of the solvent, and where the solvent may act as an addendum.

Preparation and Properties of the Sulphocyanates.

1. CUPRIDIAMMONIA SULPHOCYANATES.

This salt may be prepared by dissolving cupric sulphocyanate in dilute ammonia water, or by digesting cuprous sulphocyanate and dilute ammonia water in contact with the air;[1] also by treating solutions of potassium or ammonium sulphocyanates with ammonia water and solutions of cupric salts, provided all the solutions are "dilute."[2] The salt is readily obtained from the solutions on standing in the air or over sulphuric acid in a desiccator. It is quite pure when first separated, and is sufficiently stable to be dried in the air. Long-continued exposure to the air results in its decomposition. The salt is not soluble in water, although it has been stated that this is the case.[3] The compound appears in gray-blue needles, the color of which, when dry, is suggestive of gun-metal. Under the polarizing microscope the crystals invariably exhibit parallel extinction and the biaxial brush, so that they are probably orthorhombic. The following analysis of a specimen that had been preserved in a bottle about 6 weeks served for identification.

Salt taken for analysis. Gram.	Standard acid neutralized. cc.	Percentage of ammonia found.	Percentage of ammonia calculated for $Cu(SCN)_2.2NH_3$.
0.4723	20.64	15.86	15.95
0.4598	20.09	15.86	

2. CUPRITETRAMMONIUM SULPHOCYANATE.

This salt was first prepared by T. W. Richards and Merigold.[4] As the method they used has been shown to be unnecessarily complicated, it need not be given. The same salt is obtained when a cupric salt is dissolved in "strong" ammonia water and treated with a solution of potassium or ammonium sulphocyanate.[5]

The following conditions furnish readily a good yield of the salt: To a solution of 250 grams of crystallized copper sulphate, $CuSO_4.5H_2O$, in 800 cc. of water, warmed to about 60°, add 300 cc. of ammonia water, sp. gr. 0.9. To 162 grams of ammonium thiocyanate, in 200 cc. of water warmed to about 60°, add 100 cc. of ammonia water, sp. gr. 0.9. Mix the 2 solutions and filter rapidly. The salt separates from the filtrate within a short time.

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[1] Meitzendorff: Pogg. Ann., **56**, 92 (1842).

[2] Litterscheid: Arch. der Pharm., **239**, 336 (1901). Kohlschütter: Ber. d. chem. Ges., *loc. cit.*

[3] *Vide* Meitzendorff: *Loc. cit.*, and Litterscheid: *Loc. cit.*

[4] Z. anorg. Chem., **17**, 250 (1898).

[5] Litterscheid: *Loc. cit.*; Kohlschütter: *Loc. cit.*

The salt is very unstable in the air, and its instability is increased by small amounts of impurity. It can be recrystallized from ammonia water, sp. gr. 0.9, by cooling, or by passing a current of air rapidly through the solution. The pure, dry salt has a measurable tension of ammonia over it, so that it cannot be kept pure for any length of time in a desiccator. The following analysis of a specimen recrystallized and kept for 2 days in a tight (?) desiccator over sticks of potassium hydroxide served for identification:

Salt taken for analysis. Gram.	Standard acid neutralized. cc.	Percentage of ammonia found.	Percentage of ammonia calculated for $Cu(SCN)_2.4NH_3$.
0.5456	44.67	27.25	27.52
0.3789	31.08	27.28	

The salt has the deep, purple-blue color of cupritetrammonium sulphate. It is soluble in water, but the dissolved salt is decomposed by great dilution with precipitation of a basic salt. The salt has been described as appearing in "rhombic plates." Its rapid decomposition makes its microscopic examination difficult, but it exhibits parallel extinction and a uniaxial interference figure. Some large crystals obtained from a solution that was losing ammonia very slowly confirmed the opinion that the crystals are hexagonal, and showed that they belong to the trapezohedral group.

EXPERIMENTAL METHODS.

The saturated solutions in the solubility determinations were made under conditions that have been described. Five hours' shaking usually sufficed for attaining equilibrium, though the solids were shaken with the solutions from 6.5 to 7.5 hours.

The saturated solutions were analyzed volumetrically.

In determining ammonia, quantities of the saturated solutions, from 2 to 5 cc., were weighed in 50 cc. measuring flasks and, after partial dilution, were treated with a little zinc dust. The copper is removed very rapidly, at ordinary temperatures, by the finely divided zinc. Each colorless solution thus obtained was diluted to the mark, shaken thoroughly and filtered through a small filter into a 25 cc. burette, due care being taken to discard the first filtrates. The titration was then made against a standard sulphuric acid, using methyl orange as indicator.

In determining thiocyanic acid, weighed quantities of the saturated solutions were analyzed by Volhard's method. This method had been used in ammoniacal copper solutions by Richards and Merigold.[1] There is no difficulty in its employment provided an excess of the standard silver nitrate is always added to the ammoniacal solutions before the excess of ammonia is neutralized with nitric acid. The silver nitrate solution was standardized by weighed quantities of cupridiammonium sulphocyanate, dissolved in ammonia water.

The distillation in the analysis of a cuprammonium salt for ammonia has been completely freed from "bumping" by adding some granulated tin, an effect more or less accomplished by the addition of lime[2] in our earlier analyses. The satisfactory action of the tin is independent of the presence of the copper that deposits on it when a cuprammonium salt is analyzed. Aluminium and zinc are not good substitutes for the tin because of the rapidity with which they react on the alkali. A comparison of the duplicate analyses of the sulphocyanates gives a fair idea of the accuracy attainable by the method when tin is used.

The specific gravity determinations were made by weighing a glass sinker, belonging to a Westphal balance, in freshly boiled water and in the saturated solutions, at 25°. The saturated solutions were placed in a narrow measuring cylinder that was always filled to the same mark, so that the fine wire suspending the sinker was always wet by the solutions to about the same extent. During a weighing the cylinder stood in the center of a large beaker of water at a temperature of 25°. The cylinder and beaker were kept in the thermostat when not in use, and the weighings were made as soon as possible after their removal from the thermostat. A large analytical balance was used. This method is capable of giving results that are accurate to the sixth decimal place.[1]

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[1] *Loc. cit.*

[2] THIS JOURNAL, 32, 255 (1904).

CHEMICAL LABORATORY,
BRYN MAWR COLLEGE,
November, 1906.

INFLUENCE OF SOLVENTS IN THE CLAISEN CONDENSATION; CATALYTIC ACTION OF ETHER AND OF TERTIARY BASES IN THIS REACTION AND ALSO IN THE FORMATION OF THE GRIGNARD REAGENT.

(PRELIMINARY COMMUNICATION.)

BY J. BISHOP TINGLE AND ERNEST E. GORSLINE.

In a paper read in abstract before the American Chemical Society, at the New York meeting last December, we stated that we had obtained evidence which pointed to a specific action on the part of the solvent on the course of the Claisen condensation. We have now accumulated a number of observations bearing on this subject, all of which point to the *complete parallelism of the Claisen and Grignard reactions, so far as the effect of solvent is concerned.* We find that certain reactions, such for example as that between ethyl oxalate and camphor, take place readily and, apparently, with practically equal ease in ligroin or in ether solution. Others, such as that between ethyl phthalate and camphor, require many hours or days in ligroin solution, but take place easily when the materials are dissolved in ether. If a little ether be added to the ligroin solution, reaction begins at once and proceeds to completion. Apparently, the time required to carry the reaction to an end is dependent, other things being equal, on the amount of ether added. The position, then, is this, *we can accelerate or retard*

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[1] Kohlrausch: Wied. Ann., **50**, 118 (1893); **53**, 15 (1894); **56**, 185 (1895).

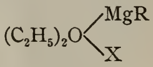
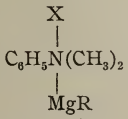
a given condensation by adding or withholding ether from the solution.

The question at once arises, is this change in the velocity of the reaction due to a difference in the solvent action of the ether, or ether-ligroin mixture, as compared with the ligroin alone, or is it due to a difference of the temperature at which the reactions were carried out? With regard to the last point we may say that all our ligroin boiled at 36°, so that experiments carried out at its boiling point were practically at the same temperature as those carried out at the boiling point of ether. Actually, however, the majority of the experiments were performed at the temperature of the room. Moreover, we find that, under otherwise similar conditions, the time and temperature factors are inversely proportional, *i. e.*, a reaction which requires days for completion at the ordinary temperature, will be finished in a few hours if the temperature is raised to that of the boiling point of the solvent. The yield of the condensation product is practically the same in the two cases. In all our experiments, unless otherwise stated, we used sodium wire as the condensing agent. It is, perhaps, hardly necessary to add that, before use, all our solvents were treated with sodium wire until they ceased to react with it.

We may now take up the question of the solvent action of ether and ligroin. Camphor and all of the esters we employed dissolve in each solvent with great and, apparently, equal readiness, and the same is true of the condensation products, consequently the difference of solubility, if it exists, must be concerned with the sodium salts formed during the condensation of the ketone and ester. We have paid a good deal of attention to this point and have observed that the substances formed on the sodium wire sometimes flake off as rapidly as they are produced, and become partly suspended and partly dissolved in the liquid; often there is a deposit of this material on the bottom of the flask, frequently, however, it is all, or practically all, in solution. Sometimes the sodium wire becomes thickly incrusted with a hard, rough coating of a salt, which clings to the metal and retains the general shape of the original wire. Contrary to our expectations, the formation of this substance does not materially protect the sodium from being attacked by the reagents, nor does it adversely affect the yield of condensation product. Examination of the incrusted material will show that it often contains a minute thread of metal.

These differences appear to depend upon extremely subtle changes in temperature, speed of reaction, etc., and it is impossible for us to define exactly the conditions necessary for obtaining any given result, though all of them will be observed if a considerable number of condensations is carried out. In some instances, moreover, the sodium salt formed remains incrusted over the wire and retains the wire form when examination shows that all the sodium has disappeared. The interesting point in this connection is that the *yield of condensation product is essentially the same whether the sodium compound dissolves in the liquid, is suspended in it, or forms a crust over the sodium wire.* In order to cast a little additional light on the subject we prepared a concentrated solution of sodium ethylate in alcohol. Equal volumes of ether, ligroin, benzene and toluene were mixed with separate, equal quantities of this alcoholic solution; in no case was a precipitate or turbidity formed. As is well known, sodium ethylate free from alcohol is practically insoluble in ether or ligroin, but this fact has no direct bearing on our experiments. Having now determined the influence of all the factors which we thought likely to affect the result, and having established, thereby, the specific action of ether as an accelerator of the condensation, we turned our attention to the discovery of other substances which might exert a similar influence. Two of these we found to be pyridine and quinoline, which appear to be about equal in their efficiency. Their influence is quite well defined, though it is not as great as that of ether. We have carried out experiments in ligroin solution, adding a little of each tertiary base and have also made condensations with pyridine alone as the solvent. The results were similar in all cases. Furthermore, we believe that we have evidence showing that, in the case of condensation compounds capable of existing in both the enolic and the ketonic forms, the use of pyridine or quinoline in the course of their formation leads to a disturbance of the ordinary equilibrium in favor of the production of the ketonic form. This is one of the points which is, at present, under investigation; should it prove to be substantiated we may expect that it will be of considerable importance in the preparation of the class of bodies in question.

One of the theories regarding the course of the Claisen condensation postulates the formation of sodium ethylate as the first step; this is supposed to undergo certain changes resulting, finally, in the elimination of 2 molecules of alcohol for each molecule of sodium ethylate added. In this manner it has been sought to explain the gradual acceleration of the reaction leading to the production of ethyl acetoacetate. Should this hypothesis be correct it is evident that sodium ethylate itself should be an excellent accelerator. This we have found to be the case. The addition of a few drops of absolute alcohol, saturated with sodium, to a mixture of ligroin, ethyl acetate and sodium wire immediately starts a reaction. A comparison experiment showed that alcohol itself assisted in promoting the action of the sodium, to an extent even greater than that exhibited by sodium ethylate. In presence of the latter the sodium wire was immediately darkened and the reaction continued steadily to the end. With the absolute alcohol the sodium wire remained entirely unattacked for nearly 5 minutes; a white compound was then formed in small quantity, and immediately thereafter a darker colored product. The reaction now proceeded rapidly and was apparently completed much sooner than when sodium ethylate was used. These experiments were carried out with camphor and ethyl phthalate, in ligroin solution. It may be added that in the course of a large number of experiments performed with various esters and condensing agents, we have never obtained a good yield of condensation product if we found it necessary to add alcohol in order to bring the sodium into solution. This is in entire accord with Claisen's experience. He found that sodium ethylate, in alcoholic solution, was the least active condensing agent. This point is at present under investigation.

In a series of papers of great interest, W. Tschelinzeff[1] has shown that the Grignard reagent is probably an oxonium derivative, that at all events, as usually prepared, it contains ether as an integral part of the molecule. He has also demonstrated that certain tertiary bases, such as dimethylaniline, can take the place of the ether and, further, that although, in the absence of ether or of a tertiary base, the formation of the Grignard reagent does not take place at the temperature of boiling ether, yet it does so if the temperature be sufficiently raised, say to that of boiling benzene or toluene. He points out that both the ether and tertiary base act as typical catalytic agents in this reaction, and gives the formulas  $(C_2H_5)_2O\!<\!{}^{MgR}_{X}$ and  $\overset{\overset{X}{|}}{\underset{\underset{MgR}{|}}{C_6H_5N(CH_3)_2}}$ as representing the probable constitution of the MgR ether compound and that of the tertiary base, respectively. It is at once evident that there is a close analogy between our results with the Claisen reaction and those of Tschelinzeff with the Grignard reagent. Accordingly, we have carried out a number of experiments to clear up certain points regarding which information was not available.

Our conclusions may be briefly summarized as follows: The rapidity with which the magnesium is attacked by the halide compound is dependent on the nature of the alkyl or aryl halide employed, provided, of course, that other conditions remain constant. The presence of ether is not essential to the reaction, *neither is a high temperature necessary, provided that sufficient time be allowed.* A number of our experiments were carried out at the ordinary room temperature, in ligroin solution (b. p. 36°). The Grignard reaction admits of being controlled with the greatest ease; as is well known, its velocity can be increased by the use of ether, a tertiary base (pyridine, quinoline, etc.), or iodine, or by means of a high temperature (see above). The use of low-boiling ligroin, on the other hand, quickly diminishes the speed of reaction. In short, then, we appear to have a *complete analogy in behavior between the Claisen reaction and the formation of the Grignard reagent.*

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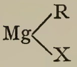
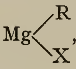
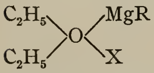
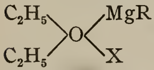
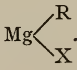
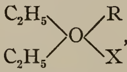
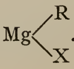
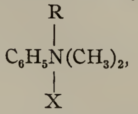
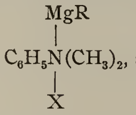
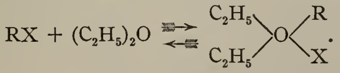
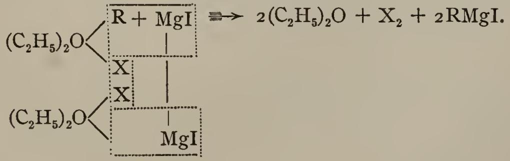
[1] Ber. d. chem. Ges., **37**, 2081, 4534; **38**, 3664 (1905). Cf. Tingle: THIS JOURNAL, **35**, 94 (1906).

As regards the theory of the latter, we should like to offer a few remarks which will follow the same general lines as the ideas of Tschelinzeff, although there are one or two points which we think are not made quite clear in his paper. The reaction Mg + RX $\rightarrow$  $\mathrm{Mg}{<}^{R}_{X}$ takes place with more or less difficulty, depending on the factors referred to above. Grignard's reagent has the formula  $\mathrm{Mg}{<}^{R}_{X}$, *i. e.*, ether is *not* an essential constituent. The reaction represented above is greatly accelerated by the presence of a little ether, which acts as a catalyst, forming an oxonium compound such as  $\frac{C_2H_5}{C_2H_5}{>}O{<}\frac{MgR}{X}$ (Tschelinzeff). Evidently, however, this is *not* the compound which *necessarily* reacts with the aldehyde, ester, etc., in the Grignard condensations; although, of course, in presence of excess of ether it might be capable of doing so, it must, therefore, be an intermediate compound, in equilibrium, as represented by the equation: Mg + RX + $(C_2H_5)_2O$ $\rightleftarrows$  $\frac{C_2H_5}{C_2H_5}{>}O{<}\frac{MgR}{X}$ $\rightleftarrows$ $(C_2H_5)_2O$ +  $\mathrm{Mg}{<}^{R}_{X}$. The question now arises, to what is the acceleration of the ether due. As it is difficult to see how it can have any effect on the magnesium metal, we can only regard it as favoring the dissociation of the alkyl halide into R + X and, since the question is not one of dilution, we see no escape from the conclusion that it forms the oxonium compound,  $\frac{C_2H_5}{C_2H_5}{>}O{<}\frac{R}{X}$, which would certainly be unstable and would, therefore, in all probability, unite quickly with the magnesium to form  $\mathrm{Mg}{<}^{R}_{X}$. In support of this theory of ours we may point out that the corresponding reaction with a tertiary base, leading, in the case of dimethylaniline, to the production of the compound,  $C_6H_5N(R)(X)(CH_3)_2$, is exactly what we expect from such substances, whereas, to say the least, a compound,  $C_6H_5N(MgR)(X)(CH_3)_2$, as formulated by Tschelinzeff, is very unusual and without any special analogy. A further point for consideration is the effect of the trace of iodine which is so frequently added to start the attack on the magnesium. In view of the work of Baeyer and Villiger,[1] it can hardly be doubted that a magnesium subiodide, such as Mg_2I_2, is first produced and that this then reacts with the oxonium compound formulated above. Of course the magnesium is often attacked directly by the halide compound; to what extent this occurs obviously depends on the nature of the latter. To sum up, then, we regard the acceleration in the formation of the Grignard reagent as dependent on such actions as are represented by the equations:

(1) $Mg_2 + I_2 \rightarrow IMg.MgI.$

(2) 

$RX + (C_2H_5)_2O \rightleftharpoons (C_2H_5)(C_2H_5)O(R)(X).$

(3) 

Almost ever since the discovery of ethyl acetoacetate the mechanism of its formation has been a matter of controversy. The investigation of the Claisen condensation, of which the reaction in question is a special case, so far from settling the matter, appeared to rouse the combatants to greater efforts and more vigorous language. During the past 10 years the dispute has been carried on chiefly by Claisen, Michael and Nef, each of whom had a particular theory to support. Quite recently Professor Nef has announced[1] that he has abandoned his own theory in favor of that of Claisen. It is but just to say that he is, apparently, at present, at least as emphatically in favor of Claisen's theory as, heretofore, he has been against it and that he now appears to be just as certain that Claisen is right and Michael is wrong as, in the past, he has been prepared to demonstrate, beyond question, that they were both absolutely in error. To us, and we believe to most chemists, the only thing about the matter which is beyond dispute is that when three investigators of the eminence of Messrs. Claisen, Michael and Nef disagree on a question, it may be taken as certain that the experimental data are necessarily inadequate to support any theory.

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[1] Ber. d. chem. Ges., 36, 2775 (1903). Cf. Tingle: THIS JOURNAL, 35, 95 (1906).

It would be easy for us to put forward a more or less attractive looking scheme of equations which could be made to include many fanciful dissociations and be in accord with our own work; we have not done so because we believe that such an attempt is premature in the present state of knowledge of the subject. Nevertheless, we desire to emphasize the fact that any hypothesis which may be put forward in the future will have to take account of the *accelerating action of ether and of the tertiary bases, and also of the similarity between the Claisen reaction and the formation of the Grignard reagent.*

EXPERIMENTAL.

The following experiments were carried out with camphor (1.5 mol.), unless otherwise stated. The proportion of sodium wire was 1 atom and of the particular ester 1 molecule.

1. No apparent action takes place on adding camphor, dissolved in ethyl benzoate, to sodium dissolved in absolute alcohol (4 mol.). After remaining for some hours the mixture was heated on the water-bath for 2 hours. A light colored

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[1] THIS JOURNAL, **37**, 302 (1907).

precipitate formed which gradually settled as a dark cake on the bottom of the vessel. Treatment with ice water, followed by acidification, gave unchanged ethyl benzoate. No condensation compound could be detected. This experiment shows how *slight* is the *condensing power of sodium ethylate*; the following 2 demonstrate the *effect of temperature.*

2. Ethyl benzoate and camphor, with sodium wire and ligroin (b. p. 36°), were mixed at the ordinary room temperature. After 48 hours, without heating, the sodium had almost entirely disappeared. In another experiment the time required was 5 working days.

3. In this experiment the mixture was heated on the water-bath to the boiling point of the solvent. After 2 hours action appeared to be complete, but the mixture was allowed to remain over night. The yield was practically the same as in 2.

Experiment 4 proves the effect of *differences in the ester.*

4. Ethyl oxalate, under conditions given in 2, reacts vigorously in a few minutes, without external heat. The yield was essentially the same as usual.[1]

The result of differences in the *constitution of the ketone or aldehyde* employed is sufficiently evident from Claisen's work, so that we paid no particular attention to this point.

Our next experiments were directed to prove that *the solvent* exercises a *decided effect on the progress of the reaction.*

5. Experiment 2 was repeated, except that to the 400 cc. of ligroin 100 cc. of absolute ether were added. The wire quickly darkened and became rough, and a dark mass collected at the bottom of the vessel. At the end of 3 hours, without heating, the action was complete and an excellent yield of condensation product was obtained. This, taken in conjunction with the second experiment, not only proves the question of acceleration, but also shows that the action is *not due* to *increased solubility* of any sodium salt in the ether-ligroin mixture, as compared with ligroin alone.

Experiments 6 and 7 demonstrate the result of the addition of *pyridine* and *quinoline*, respectively, in place of ether.

6. The conditions were similar to Expt. 5, but 75 cc. of

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[1] *Vide* Bishop Tingle: THIS JOURNAL, 19, 393 (1897); **20**, 218 (1898).

pyridine were added in place of the ether. The liquid rapidly darkened and behaved essentially as in the previous case. The reaction appeared to be complete in about 12 hours. The yield was poor.

7. In this case the pyridine was substituted by 20 cc. of quinoline. Action commenced at once, the liquid depositing a dark brown substance in the usual manner. The mixture was heated to boiling for 2 hours, at the end of which time the action was finished. The yield was good.

The influence of *sodium ethylate* or of *absolute alcohol, in small quantity*, is shown by Expts. 8 and 9.

8. Experiment 7 was repeated, but in place of the quinoline there was added 50 cc. of absolute alcohol saturated with sodium ethylate, *i. e.*, treated with the metal until the latter remained undissolved. The liquid darkened at once, the wire became coated and after 10 minutes the contents of the flask began to boil quietly. After 30 minutes the wire had completely disintegrated. The yield of condensation product was very poor, but a relatively large quantity of benzoic acid was obtained.

9. This was essentially the same as Expt. 8, except that for the sodium ethylate solution there was substituted an equal volume of absolute alcohol. The action was complete in 15 minutes and, as in the previous case, a red mass settled to the bottom of the vessel.

We have carried out experiments with camphor and ethyl phthalate similar to Expts. 2, 5, 7, 8 and 9 recorded above for ethyl benzoate. In general, the results were entirely analogous; the chief difference is that ethyl phthalate reacts rather more readily than ethyl benzoate. In a further experiment we tried the effect of adding 2 drops of sodium ethylate solution, as above, to the substances dissolved in 200 cc. of ligroin. The reaction was, of course, not so rapid as in those experiments where a larger quantity was added, but its accelerating action was more marked than that of 10 cc. of quinoline or 25 cc. of ether, under similar conditions. The yield was, however, *markedly less*, only about half of that obtained by the use of ether or of quinoline, or when no accelerator is employed.

We have also studied the condensation of ethyl acetate to ethyl acetoacetate. By dissolving the ester (17.6 grams) in ligroin (b. p. 36°, 200 cc.) and adding the sodium wire, the reaction proceeds very slowly and was not completed after 6 hours' boiling; indeed, some wire remained undissolved after 5 days' subsequent standing, at the ordinary temperature. In contrast with this the addition of 75 cc. of ether caused the disappearance of the sodium after 2 hours' heating. Pyridine (50 cc.) acted in almost exactly the same way. The use of 5 drops of sodium ethylate solution once more demonstrated how rapidly this substance stimulates a reaction. After 0.5 hour at the ordinary temperature and 1 hour's heating, the sodium had nearly all dissolved. The ethyl acetoacetate was separated and identified in the usual manner, by the ferric chloride test and by fractionation under reduced pressure.

EXPERIMENTS ON GRIGNARD'S REACTION.

Ethyl chloracetate, in ethereal solution, reacts very vigorously with magnesium. In ligroin (b. p. 36°) solution, on the other hand, no change was apparent after 3 hours' boiling. The addition of a fragment of iodine, followed by boiling for 10 hours, caused the production of a quantity of light yellow material. The experiment was repeated, 10 cc. of ether being used in addition to the ligroin. There was no change after 3 hours' boiling, but when a fragment of iodine was added a rather vigorous action began, the light yellow solid collecting in fairly considerable quantity. This demonstrates the *formation of Grignard's reaction at 36°.*

Experiments were now carried out with ethyl iodide (7.8 grams), magnesium (1.22 grams), ligroin (500 cc.) and quinoline (30 cc.). There was no evident action on standing at the ordinary room temperature, but the magnesium was almost completely dissolved after boiling during 20 minutes. The experiment was repeated, ether (25 cc.) being substituted for the quinoline. In this case the reaction began vigorously in the cold and the liquid soon commenced to boil.

Further experiments were carried out with pyridine in the place of quinoline, the results being essentially similar to those described above.

Our work is being continued in several directions and we hope to communicate further results, together with fuller experimental details, in a subsequent paper.

JOHNS HOPKINS UNIVERSITY,
BALTIMORE, MARYLAND,
April, 1907.

Contributions from the Sheffield Laboratory of Yale University.

ON THE MOLECULAR CONDITION OF SALTS DISSOLVED IN A FUSED SALT.

BY H. W. FOOTE AND L. H. LEVY.

The lowering in the freezing point of a fused salt, caused by comparatively large percentages of a second salt, has been determined in a great many cases. The accurate determination of the lowering in freezing point of a salt caused by the addition of small amounts of another, has been difficult on account of the high melting points of most salts. It has seemed to us, however, that just such a determination would have some interest as we might expect the laws for dilute solutions to apply in this case. For this reason we have undertaken to determine accurately the lowering in the freezing point of sodium chlorate, caused by small amounts of other salts in solution.

The melting point of sodium chlorate is only 255°. Differences in temperature at this melting point can be determined with a considerable degree of accuracy with the ordinary Beckmann thermometer, as we have convinced ourselves by many experiments. The salt can be obtained in very pure condition indeed, it is a good solvent for other salts and its tendency to supercool without freezing is very slight. This salt appeared, on the whole, to be the best for our purposes and it has been used as a solvent in our experiments.

From the experimental data which are given below we have calculated the molecular weights of a considerable number of salts containing a radical in common with sodium chlorate. The results are discussed later.

The molecular weights were calculated from the well-known formula,

$$M = \frac{ks}{\Delta L},$$

in which M = the molecular weight, s = the weight of dissolved substance, Δ = the lowering in the freezing point of the solvent, L = the weight of the solvent, and k is the constant for sodium chlorate. To obtain the constant k, the heat of fusion of sodium chlorate was determined. The constant was then calculated from the van't Hoff formula,

$$k = \frac{2T^2}{\lambda},$$

in which T = the absolute melting point and λ the heat of fusion in calories of 1 gram of sodium chlorate. The heat of fusion was calculated from determinations of the amount of heat evolved by sodium chlorate in a water calorimeter when this salt had been heated at 2 temperatures above the melting point and at 2 temperatures below. The specific heats of sodium chlorate slightly above and below the melting point could be calculated by this method and the heat of fusion determined from the formula:

$$\lambda = Q - c_1(t_a - t_s) - c_2(t_s - t_b) - H.^1$$

In this formula,

λ = heat of fusion of 1 gram sodium chlorate.

t_a, t_b = respectively, temperatures slightly above and below the melting points of sodium chlorate.

t_s = melting point of sodium chlorate, 255.°.

c_1, c_2 = respectively, the specific heats of liquid and solid sodium chlorate near the melting point.

Q = heat evolved by 1 gram of sodium chlorate cooled from temperature t_a to 22°.

H = heat evolved by 1 gram of sodium chlorate cooled from temperature t_b to 22°.

For the determinations, fused sodium chlorate, which had been recrystallized, was poured into capsules holding 50–60

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[1] Cf. Ostwald-Luther: Physico-Chem. Messungen, p. 206.

grams. The capsules were made of brass, silver, or platinum, and the results were practically independent of the metal used in the capsule after a correction was introduced for the heat evolved by the metal. The cover to the capsule was not quite water-tight, so the joint was covered, while the capsule was hot, with linseed oil which had been boiled till it was very thick. This made a hard enamel on cooling and made the brass capsule perfectly tight. The other capsules always admitted a small amount of water when cooled in the calorimeter, but the very small error introduced here, due to the heat of solution, could be disregarded. The capsules, filled with a weighed quantity of sodium chlorate, were heated at the temperature desired for 2 hours or more, in a glass tube which was kept in a low-fusing bath whose temperature could be kept constant within 1°. This bath was made of about equal parts of sodium and potassium nitrates and sodium nitrite. It fused below 200° and served its purpose admirably here as well as in the determination of the lowering of the melting point. The bath was fused in a "granite-ware" kettle and was stirred continuously during an experiment. When the capsules were to be heated above the melting point of sodium chlorate, the temperature was raised at first considerably higher than the temperature desired, to be sure of complete melting, and then it was lowered to the point required. After heating, the capsule was removed quickly from the heating tube and plunged in the calorimeter. The operation required not more than 1 or 2 seconds. The calorimeter was a large one, kindly loaned us by Prof. W. G. Mixter, who has already described it.[1] It had a heat capacity of 50 calories and held about 3 kilos of water. The amount of water used was determined by weighing on a balance, which weighed several kilos with an error of a few milligrams. The temperature of the calorimeter was adjusted before each experiment so that the temperature, after the capsule was introduced, should be approximately 22°. The calorimeter was stirred with a small screw propeller, which was driven by a water-motor running with compressed air. A series of readings was taken before and after the capsule was introduced and the corrected difference in temperature extrapolated in the usual manner. The heat evolved by the empty capsules was determined by experiment instead of calculating this value from the known specific heats.

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[1] Amer. J. Sci., 16, 214.

The heat evolved by 1 gram of sodium chlorate, cooling from the temperature t to 22°, was calculated from the expression,

$$\frac{h\Delta - \mathrm{R}}{\mathrm{L}},$$

where h = the heat capacity of the calorimeter and water contained in it.

Δ = rise in temperature of the water.

R = heat evolved by the metal capsule containing the chlorate.

L = weight of chlorate.

In the following table the experimental data are given, together with the calculated result for the heat evolved by 1 gram of sodium chlorate:

Table I.

Capsule.	Temp.	*h*.	Δ.	R.	L.	Heat evolved.
Brass No. 1	272	2852	2.443	1267	48.2	118.5
Platinum	268	2814	2.276	214	52.5	117.9
Brass No. 1	259	2954	2.226	1202	48.2	111.5
" No. 2	259	2980	2.318	1331	49.7	112.2
Platinum	246.5	2997	1.266	195	61.3	58.7
Silver	246.5	2990	1.312	530	57.5	59.0
Platinum	246.5	2987	1.291	195	62.4	58.7
Silver	246.5	3000	1.285	530	56.5	58.8
Brass No. 2	221	2856	1.248	1006	49.7	51.5
" No. 1	220.5	2852	1.219	991	48.2	51.6
Silver	220.5	3014	1.171	466	59.7	51.3

The specific heats, c_1 and c_2, of liquid and solid sodium chlorate are readily calculated from the results in the last column. They are:

$$c_1 = 0.581,$$

$$c_2 = 0.281.$$

The heat of fusion can now be calculated from the formula previously given:

$\lambda = 111.85 - 0.581(259^\circ - 255^\circ) - 0.281(255^\circ - 246.5) - 58.5;$

$\lambda = 48.4$ *calories.*

Substituting this value in the van't Hoff formula,

$$k = \frac{2T^2}{\lambda},$$

$$k = \frac{2 \times (528)^2}{48.4} = 11500.$$

The Beckmann freezing point apparatus, with some modifications to fit our conditions, was used to determine the lowering of the freezing point. The freezing bath consisted of the same mixture of sodium and potassium nitrates and sodium nitrite which was used in determining the heat of fusion of sodium chlorate. The bath was held at 249°–250° by regulating the gas supply and stirring the mixture thoroughly. The bath weighed several kilos, so that the temperature changed but slowly, and it was an easy matter to hold it nearly constant. The outer freezing jacket of the Beckmann apparatus dipped into the bath, and the inner freezing tube containing the chlorate, fitted into the jacket, leaving an air space between. A second smaller bath was heated considerably above the melting point of sodium chlorate and was used to melt the chlorate before the freezing point determination was made.

Assuming that the value of a degree, as registered by a Beckmann thermometer, is correct for 20° C., the value is too small for higher temperatures, since mercury is removed from the bulb and not as much mercury is left to expand. The correction is very small for ordinary boiling and freezing point determinations and is usually neglected. At 255°, however, the freezing point of sodium chlorate, this error is not negligible and we have introduced a correction. If q represents the value of 1° on the Beckman thermometer, at 250°, compared with the value at 20°, and α represents the coefficient of expansion of mercury in glass,

$$\text{then } q=\frac{1+20\,\alpha}{1+250\,\alpha}.$$

For α we have used the value 0.000157, so that

$$q = 0^\circ.965.$$

The observed lowering of the freezing point of sodium chlorate has been corrected throughout by dividing by this value, 0.965.[1]

For each experiment, about 30 grams of sodium chlorate in a freezing tube were placed in the melting bath until the salt fused to a clear liquid. The tube was then transferred quickly to the freezing bath and the freezing point determined. Every freezing point was determined 2 or 3 times, the chlorate being completely melted between each reading. Duplicate readings on the pure chlorate and on the solutions seldom differed from each other more than 0°.01. Weighed quantities of salt were added to the chlorate, dissolved by thorough stirring and the freezing point determined after each addition.

Fused sodium chlorate shows a slight tendency to supercool. By stirring regularly before the freezing point was reached the supercooling did not exceed 0°.2–0°.3 and the temperature rose quickly to the freezing point when freezing began. No correction was applied for the additional concentration of the solution due to the separation of the solid.

The molecular weight was calculated from the formula given previously,

$$M=\frac{ks}{\Delta L}.$$

Every series of determinations was duplicated. Several sodium salts could not be used. Sodium sulphate and tetraborate were too insoluble. Sodium iodide and dichromate decomposed in the melted chlorate. Of the salts which were used, sodium fluoride and chloride were difficultly soluble, the fluoride especially so. The results are given in the following table. The theoretical molecular weight is put in parenthesis after the formula of the compound. The symbols at the head of the columns are those used in the molecular weight formula:

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[1] Ostwald-Luther: Phys. Chem. Meas., p. 291.

Table II.

L.	*s.*	Grams solute in 1000 grams solvent.	Δ.	M.
		NaCl (58.5).		
28.544	0.0832	2.92	0.534	63
"	0.2481	8.69	1.570	64
30.215	0.1478	4.89	0.833	67.5
"	0.2561	8.48	1.473	66
		$NaNO_3$ (85).		
32.393	0.1625	5.33	0.637	91
"	0.2899	8.95	1.124	92
37.393	0.9629	25.75	3.062	97
30.300	0.2026	6.69	0.855	90
"	0.4063	13.41	1.696	91
"	0.7024	23.18	2.893	92
		NaBr (103).		
29.565	0.3000	10.15	1.129	103
"	0.8051	27.23	2.980	105
30.000	0.4002	13.36	1.461	105
"	0.6614	22.06	2.401	105
"	1.1945	39.82	4.238	108
		Na_2CO_3 (106).		
30.025	0.0340	1.13	0.107	121
"	0.1113	3.71	0.355	120
"	0.3503	11.66	1.133	118
30.195	0.0543	1.80	0.183	113
"	0.3074	10.18	1.043	112
40.195	0.6209	15.45	1.673	106
		Na_2CrO_4 (162).		
30.120	0.1605	5.33	0.379	162
"	0.3766	12.50	0.890	162
"	1.2298	40.84	2.790	168
30.305	0.2310	6.05	0.541	162
"	0.3736	12.34	0.873	162
		NaF (42).		
30.615	0.1253	4.09	1.078	44
"	0.1926	6.29	1.501	48
30.040	0.1093	3.64	0.935	45

Table II (Continued).

$KClO_3$ (122.6).

L.	*s*.	Grams solute in 1000 grams solvent.	Δ.	M.
29.981	0.1742	5.81	0.497	134
"	0.5455	18.19	1.565	134
"	0.9002	30.03	2.591	133
30.185	0.421	13.94	1.209	132
"	1.1898	39.42	3.330	136
"	1.3770	45.62	3.857	136

$CsClO_3$ (216).

L.	*s*.	Grams solute in 1000 grams solvent.	Δ.	M.
30.240	0.2290	7.57	0.403	216
"	0.6893	22.79	1.225	214
30.595	0.2430	7.94	0.427	214
"	0.7266	23.75	1.305	209

$Ba(ClO_3)_2$ (304.4).

L.	*s*.	Grams solute in 1000 grams solvent.	Δ.	M.
29.828	0.6962	23.34	0.839	320
"	1.2639	42.37	1.523	320
"	1.7641	59.15	2.104	323
30.280	0.6289	20.77	0.765	312
"	1.3296	45.87	1.595	317
"	3.2069	105.66	3.819	319

Taken as a whole, the results show very nearly normal molecular weights. In every case but one the molecular weights are slightly higher than the calculated values. While this may be due to slight polymerization, or, especially in the case of potassium chlorate, to a slight tendency to form mixed crystals, we are inclined to believe that the high values are due either to a small error in determining the heat of fusion, which would affect the value of the constant in the molecular weight formula, or to the fact that the gas laws do not hold with great accuracy in the solutions. The determination of the heat of fusion was not by any means a simple matter. The results, we believe, prove that *salts dissolved in fused sodium chlorate show no appreciable tendency toward polymerization.*

On the other hand, although the molecular weights calculated indicate no dissociation, the results can equally well be explained by assuming that dissociation is present. If pure fused sodium chlorate is partially dissociated, the ions should lower the freezing-point, so that the pure salt would melt at a lower temperature than it would if there were no dissociation. When a salt is added with a common ion, assuming that it is largely dissociated, it would tend to repress the dissociation of the sodium chlorate, thus raising the melting point. At the same time its ions would lower the melting point and the joint effect would be the same as though neither were dissociated. This can be shown very simply in the following manner: Let x gram-equivalents of a sodium salt, such as sodium nitrate, be added to a unit volume of sodium chlorate. Assuming no dissociation, the concentration of the dissolved molecules would be x. On the other hand, let x gram-equivalents of sodium nitrate be added to the unit volume of sodium chlorate, assuming the former to be completely dissociated and the latter partially so. In the pure chlorate, if c_o represents the concentration of the sodium and the chlorate ions, by the law of mass action,

(1) $$c_o^2 = K.$$

When x gram-equivalents of sodium nitrate are added, the concentrations of the sodium and chlorate ions originally present change to new values which may be represented by c_o^1+x and c_o^1, respectively, and since the product of the ions must remain constant,

(2) $$(c_o^1 + x)c_o^1 = c_o^2.$$

If the dissociation of sodium chlorate is moderately large, x is small compared to c_o^1 and equation (2) may be simplified to

$$c_o^1+\frac{x}{2}=c_o,$$

or (3) $$c_o^1=c_o-\frac{x}{2}.$$

The total concentration of ions after x gram-equivalents of sodium nitrate were added would be:

$$\underset{\text{Na ions}}{c_0{}^1 + x} + \underset{\text{ClO}_3\text{ ions}}{c_0{}^1} + \underset{\text{NO}_3\text{ ions}}{x},$$

or the total concentration of ions becomes

$$2c_0{}^1 + 2x. \tag{4}$$

Substituting the value of $c_0{}^1$ from (3) in (4) the total concentration of ions becomes

$$2c_0 - x + 2x,$$

or

$$2c_0 + x.$$

Since the original concentration of ions was $2c_0$, it follows that the concentration of ions in the sodium chlorate has increased by x, although $2x$ ions were added. It follows that *the increase in the number of ions present, caused by adding x equivalents of a completely dissociated salt with a common ion, would be equal to the number of molecules added by x equivalents of an undissociated salt.* The depression of the freezing point would thus be the same in either case and our results give no positive information as to whether or not the dissolved salts are largely dissociated.

In the demonstration as outlined above, it was assumed that the dissolved salt was very largely or completely dissociated and that the dissociation of sodium chlorate was considerable. If the dissociation of sodium chlorate were very slight, the depression of the freezing point would be greater when the dissolved salt was dissociated than it would be if undissociated. This is the case with solutions in water, as is well known.

An experiment was tried to show that both solvent and solute could not be very largely dissociated by comparing the depression of the freezing point caused by potassium nitrate or potassium chloride with that of sodium nitrate, the latter containing an ion in common with sodium chlorate. If neither solvent nor solute dissociate, the reaction

$$NaClO_3 + KNO_3 = NaNO_3 + KClO_3$$

should be very nearly complete when potassium nitrate is dissolved in an excess of sodium chlorate, on account of the mass action of an excess of sodium chlorate. For every molecule of potassium nitrate added, therefore, 2 other molecules are formed. By dissolving an equivalent amount of sodium nitrate in sodium chlorate double decomposition is impossible, so that the lowering of the freezing point in the first case should be double that in the second. If both solvent and solute were largely or completely dissociated there would be no chance for reaction in either case, as may be seen if we write the substances in the form of ions:

$$Na + ClO_3 + K + NO_3;$$
$$Na + ClO_3 + Na + NO_3.$$

The depression should, therefore, be the same whether sodium or potassium nitrates were used in equivalent amounts. To obtain comparative results between the lowering caused by sodium nitrate and that caused by potassium nitrate, or potassium chloride, we have recalculated our previous results on sodium nitrate to obtain the molecular weight constant, assuming the molecular weight of sodium nitrate to be normal. The result was

$$k = 10700.$$

Using this value, the lowering produced by potassium nitrate or potassium chloride could be calculated in case it behaved like sodium nitrate, and this calculated lowering could be compared with that actually observed. The results obtained were as follows:

KNO_3.

L.	s.	Δ observed.	Δ calculated.	$\frac{\Delta \text{ observed}}{\Delta \text{ calculated}}$.
29.935	0.2730	1.922	0.963	1.996
"	0.4363	3.062	1.544	1.983
30.430	0.2210	1.579	0.770	2.05
"	0.4325	2.982	1.506	1.987
		KCl.		
30.010	0.1981	1.777	0.927	1.91
30.205	0.3084	2.792	1.904	1.90

From the ratios in the last column it will be noticed that the observed depression in each case is nearly twice the depression that would be caused if equivalent amounts of sodium nitrate were used. This would indicate that neither solvent nor solute were dissociated, instead of both being largely or completely so. The results can, however, be explained by assuming that the solute is largely dissociated and the solvent less so, by a method similar to that used previously in showing that dissolved substances may be dissociated, although the molecular weights calculated are normal.

The molecular weights of a number of chlorides and bismuth salts, dissolved in bismuth chloride, have been determined by Rügheimer[1] from vapor pressure measurements on bismuth chloride. The only salt whose molecular weight has been determined by both of us is sodium chloride. The average value found by him was 65, which is also the average of our results. The same objection may be raised to his results that we have mentioned in regard to ours, that the solvent may be somewhat dissociated and the solute largely so. The addition of the dissociated solute would repress the dissociation of the solvent, tending to raise the vapor pressure, while the ions added have the opposite effect, the result being that the vapor pressure is lowered as it would be if the molecular weight of the solute were normal.

Silver chlorate, as is well known, forms mixed crystals readily with sodium chlorate.[2] It would be expected, therefore, that when the solvent separated it would carry a certain proportion of solute with it, so that the observed depression of the freezing point would be too low and the molecular weight calculated would be high. The determinations which follow show this to be the case.

$AgClO_3$ (191.5).

L.	s.	Grams solute in 1000 grams solvent.	Δ.	M.
30.390	0.6222	20.47	0.346	680
"	0.9295	30.58	0.524	671
30.295	0.9316	30.75	0.529	669
"	1.5766	52.05	0.888	674
"	3.1449	103.8	1.720	694
"	6.2676	206.9	3.287	724
"	7.8656	259.6	4.060	735

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[1] Ann. Chem. (Liebig), **339**, 297.

[2] Z. physik. Chem., **5**, 438 (1890). THIS JOURNAL, **27**, 345 (1902).

We hope, later, to attack the problem of molecular weights in fused sodium chlorate from another side.

We wish to express our sincere thanks to Prof. W. Nernst for some very valuable criticisms and suggestions in connection with this work.

Summary.

In the present article the heat of fusion of sodium chlorate has been determined and the constant for sodium chlorate calculated in the molecular weight formula,

$$M = \frac{ks}{\Delta L}.$$

The lowering in the freezing point of sodium chlorate produced by small amounts of other salts has been determined with considerable accuracy.

The molecular weights of a number of chlorates and sodium salts have been calculated from the data obtained and found to be nearly normal.

The results indicate that there is little or no polymerization, but they do not prove that dissociation is absent, as nearly normal molecular weights would be obtained if the solute were very largely dissociated and the solvent somewhat less so.

New Haven, Conn.,
December, 1906.

Contributions from the Chemical Laboratory of the University of Illinois.

ON REVERSIBLE METALLIC DISPLACEMENTS IN AQUEOUS SOLUTIONS.

By George McPhail Smith.

INTRODUCTION.

When a metal is immersed in the solution of an electrolyte, the solution pressure of the metal tends to drive particles of it into the solution. These particles, or ions, carry positive electric charges, from which it results that the solution becomes positively charged, and the metal negatively charged. These charges give rise to a force component, which, on the one hand tends to prevent the entrance of more metallic ions in the solution, and on the other hand seeks to drive positive ions from the solution back to the metal. If the solution pressure of the metal is sufficiently high, ions of it continue to be driven into the solution, and, at the same time, the electrically equivalent quantity of other positive ions are forced in the opposite direction from the solution to the metal. Here they give up their charges and separate in the free state. This is the process which takes place, for example, when copper is precipitated from its salt solutions by zinc, or when water is decomposed by sodium.

In general, according to Nernst, to whom we owe the above conceptions, when one metal is immersed in the solution of a salt of another metal, the relation

$$\sqrt[n_1]{\frac{P_1}{p_1}} > \sqrt[n_2]{\frac{P_2}{p_2}}$$

must hold, in order that the second metal may be precipitated by the first. In this formula the index 1 refers to the first metal and 2 to the second metal; P_1 and P_2 are the electrolytic solution pressures, p_1 and p_2 the osmotic pressures of the ions, and n_1 and n_2 the valencies of the metals in question.

As a necessary consequence of this, it follows, that of any 2 metals, either can be made to displace the other from a solution, provided that the relative magnitudes of

$$\sqrt[n_1]{\frac{P_1}{p_1}} \text{ and } \sqrt[n_2]{\frac{P_2}{p_2}}$$

can be reversed under different conditions. Whether hydrogen will be evolved or not will depend on the relative magnitudes of

$$\frac{P_H}{p_H} \text{ and } \sqrt[n]{\frac{P_M}{p_M}},$$

where H refers to hydrogen and M to any metal present as such. That these conclusions are in harmony with the facts in a number of cases has been previously shown by the author.[1]

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[1] J. Am. Chem. Soc., 27, 540 (1905).

I.

THE ACTION OF THE AMALGAMS OF THE ALKALI AND ALKALI EARTH METALS ON VARIOUS AQUEOUS SOLUTIONS.

Previous Work.

As early as 1834, R. Boettger[1] prepared dilute amalgams of barium and strontium by the action of saturated solutions of their chlorides on sodium amalgam. It has since been established that this method is generally applicable for the preparation of the amalgams of metals which are more electronegative than sodium.

In 1871, Kraut and Popp[2] found that a crystalline potassium amalgam was formed when sodium amalgam was allowed to stand for several days under a strong solution of potassium hydroxide or carbonate. This displacement of potassium by sodium was long regarded as an anomaly, and Berthelot and others[3] have explained it as the necessary consequence of the greater loss of energy undergone by potassium than by sodium in the formation of their respective amalgams. That sodium might, in like manner, be displaced from its solutions by potassium does not appear to have entered their thoughts.

In 1903, G. Fernekes[4] investigated the action of sodium and potassium amalgams on various aqueous solutions. He found that solutions of sodium, potassium, barium and certain other chlorides, for example, when acted upon by sodium or potassium amalgam, evolved hydrogen more slowly than pure water. Further, he found that the retardation of the rate of liberation of hydrogen by sodium or potassium amalgam was about the same for isotonic solutions of sodium chloride and potassium chloride. He thought the theory of electrolytic dissociation was out of harmony with these results and, in his eagerness to find that theory at fault, he overlooked the obvious explanation.

In the same year, Kettembeil[5] prepared sodium amalgam by means of potassium amalgam, as follows: The electrolytes in 2 vessels, the one containing potassium amalgam under a solution of potassium hydroxide, and the other mercury, immersed in a solution of sodium hydroxide, were brought into contact by means of an inverted U-tube. The mercury, which was suspended in the sodium hydroxide solution, was then connected with the potassium amalgam in the first vessel by means of outside wires. After a few minutes the mercury was lifted out of the solution, quickly washed and then brought into contact with a strong solution of ammonium chloride. This gave rise to the formation of the characteristic ammonium amalgam, and thus proved the presence of sodium in the mercury.

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[1] J. prakt. Chem., **1**, 302 (1834).

[2] Ann. Chem. (Liebig), **159**, 188 (1871).

[3] Ann. Chim. Phys. [5], **18**, 442 (1879). Kerp: Z. anorg. Chem., **17**, 296 (1898).

[4] Disser'n. Univ. Wisconsin; J. Physic. Chem., **7**, 611 (1903).

[5] Z. anorg. Chem., **38**, 227 (1904).

Finally, in 1904, and independently of Kettembeil, it was shown by the author[1] that in the case of sodium and potassium either can be directly replaced by the other in its amalgam, by simply treating the amalgam in question with a solution of the chloride of the other metal. In a later paper[2] it was further shown that amalgams containing potassium or sodium can be obtained readily from barium amalgam by treating it with a concentrated solution of potassium or sodium hydroxide.

Constitution of the Amalgams.

In the case of the metals of the alkali and alkali earth groups, with which the present paper deals, it is practically impossible to work with the metals themselves in the presence of water. For that reason the amalgams of these metals were employed. At first, in accordance with the generally accepted view, it was supposed that, in mercurial solution, these metals existed as such, in the monatomic condition. This idea was abandoned, however, early in the course of the present work.

Recent investigators are unanimous in regarding the solid, crystalline amalgams of the alkali and alkali earth metals as definite chemical compounds.[1] The corresponding liquid amalgams, on the other hand, have generally been regarded as mercurial solutions of these metals in the monatomic condition.[2] This view appeared all the more reasonable because it agreed remarkably well with what was known of the metals in the gaseous state. It is the view still expressed in the latest books on physical chemistry.[3] In a preliminary communication, however, it has been shown by the author that this view is without experimental foundation; the experimental data point rather to the conclusion that the liquid amalgams of the alkali and alkali earth metals are solutions in mercury of compounds of the general formula MHg_m, containing only 1 atom of the amalgamated metal to the molecule. This conclusion is further borne out by the results obtained in the present investigation.

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[1] J. Physic. Chem., 8, 566 (1904).

[2] *Ibid.*, 9, 13 (1905).

According to the work of Kerp and Böttger,[5] who applied the phase rule to solutions of these metals in mercury, the solid amalgams appear to have the following compositions:

KHg_{12}, from 0°–71°; above 71° the solid phase becomes richer in alkali metal.

$NaHg_6$, from 0°–40°.5; $NaHg_5$ from 40°.5 – ±150°.

$LiHg_5$, from 0°–100°.

$SrHg_{12}$, from 0°–30°; above 30° the solid phase becomes richer in strontium. According to Guntz and Roederer,[6] however, this amalgam has the composition indicated by $SrHg_{11}$.

$BaHg_{13}$, from 0°–30°; $BaHg_{12}$, from 30°–100°.

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[1] Berthelot: *Loc. cit.* Kerp: Z. anorg. Chem., **17**, 284 (1898). Kerp and Böttger: *Ibid.*, **25**, 1 (1900). Maey: Z. physik. Chem., **29**, 119 (1899). Guntz and Ferée: Compt. rend., **131**, 182 (1900). Kurnakoff: Z. anorg. Chem., **23**, 439 (1900). Haber and Sack: Z. Elek. Chem., **8**, 245 (1902).

[2] Ramsay: J. Chem. Soc., **55**, 521 (1889). Heycock and Neville: *Ibid.*, **55**, 666 (1889); **57**, 376 (1890). Tammann: Z. physik. Chem., **3**, 441 (1889). G. Meyer: *Ibid.*, **7**, 447 (1891). Kerp: Z. anorg. Chem., **17**, 286 f. (1898). Schoeller: Z. Elek. Chem., **5**, 259 (1898). Erdmann: Z. anorg. Chem., **32**, 404 (1902). Rich and Travers: J. Chem. Soc., **89**, 872 (1906).

[3] Ostwald: "Lehrbuch," I., pp. 737, 767; II., pp. 859, 862 (1903).

[4] THIS JOURNAL, **36**, 124 (1906).

[5] *Loc. cit.*

[6] Bull. Soc. Chim. [3], **35**, 494 (1906).

The liquid phases corresponding to saturated solutions of these metals in mercury were found to contain:

Temperature.	K. Per cent.	Na. Per cent.	Li. Per cent.	Ba. Per cent.	Sr. Per cent.
0°	0.31	0.53	0.04	0.15	0.73
20°	0.47	....	....	0.32	1.02
25°	0.53	0.65	....	0.34	.....
64°.5	....	....	0.10	....	....

The solid amalgams are to be regarded as analogous to hydrated salts, *i. e.*, as being made up of a fundamental compound of mercury and alkali, or alkali earth metal, combined with various amounts of "mercury of crystallization."[1] The liquid amalgams are solutions of the solid amalgams in mercury.

Although each of the amalgams mentioned above is a definite compound of mercury with another metal, they are, nevertheless, all slowly decomposed by water, with the evolution of hydrogen and the simultaneous formation of the corresponding metallic hydroxides. The amalgamated metal, owing possibly to a partial dissociation of its mercury compound, has a certain tendency to enter the solution in the ionic condition, *i. e.*, it possesses a certain electrolytic solution pressure, and the introductory considerations may be applied to it just as if it were present in the mercury in the atomic condition.

EXPERIMENTAL PART.

Preparation of the Amalgams.

The mercury used in the preparation of these amalgams was purified as follows: First it was shaken with a dilute solution of potassium dichromate, which was acidified with sulphuric acid; it was then allowed to run in a finely divided state from the capillary end of a funnel, into a solution of 75 grams of mercuric nitrate and 75 cc. of nitric acid, sp. gr. 1.42, in 800 cc. of water. This solution was contained in an upright glass cylinder, 1.3 meters in height, such as is commonly used for the purpose. The mercury was allowed to fall through this solution several times in succession, and its purity was finally confirmed by analysis.

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[1] Berthelot, Kerp, Böttger, Kurnakoff and Maey : *Loc. cit.*

Potassium Amalgam.—This amalgam was prepared by the addition of 7 grams of potassium, in small portions, to 500 grams of mercury, which had previously been heated on the water-bath. After cooling, the amalgam was washed, dried with filter paper, and bottled. It should be kept in a small, tightly-stoppered bottle, because, in contact with a limited quantity of air, especially in a large bottle which is occasionally opened, the amalgam becomes coated with a dark layer of potassium suboxide,[1] mixed with finely divided mercury. After this has happened, the amalgam decomposes water with stormy violence and cannot be used for the following experiments. The pure amalgam decomposes water at a very moderate rate.

Sodium Amalgam.—This amalgam was prepared by adding 15 grams of sodium, in small quantities, to 1 kilo of mercury, at the ordinary temperature. The action was, in this case, very violent and the temperature rose to above 150°. After cooling, the amalgam was kneaded under water until thoroughly clean. It was then dried with filter paper and bottled. Sodium amalgam, when exposed to the action of a limited quantity of air, does not behave like potassium amalgam. It becomes coated with a thin, white deposit, but its action on water is not altered.

Lithium Amalgam.—This amalgam was also prepared directly from the elements. The lithium was obtained from Kahlbaum, and it was previously analyzed; 0.2 gram of the metal gave 0.0052 gram potassium chlorplatinate, equivalent to 0.0008 gram of potassium, and the filtrate from this, after evaporation, gave a faint sodium spectrum which did not last 3 seconds. The lithium was, therefore, exceptionally pure.

Two grams of lithium and 500 grams of mercury were heated together in a small flask at 220°, in a paraffin bath. On stirring, the mixture exploded and the flask was shattered. Most of the amalgam, however, fell into the bath, where it was protected from oxidation by the paraffin. It was removed after cooling and bottled. Analysis:

100 grams of the amalgam gave Li_2SO_4 0.2974 gram.

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[1] Cf. Moissan: "Traité de Chimie Minérale," III., 70.

It contained, therefore, 0.038 per cent of lithium.

Lithium amalgam decomposes water more rapidly than either sodium or potassium amalgam. It is also much less stable in the presence of air.

Barium Amalgam.—This amalgam was prepared by stirring 500 grams of sodium amalgam, for periods of 5 minutes, with 5 successive portions, of 50 cc. each, of saturated barium chloride solution, at 90°. The amalgam was then shaken for a few seconds with very dilute hydrochloric acid. Finally, it was allowed to stand for 5 hours, with occasional shaking, under a strong solution of barium chloride, containing a little barium hydroxide. The resulting amalgam was diluted with mercury. Analysis:

50 grams of the product gave $BaSO_4$ 0.7835 gram and Na_2SO_4 0.0032 gram.

It therefore contained 0.922 per cent of barium and 0.002 per cent of sodium.

Strontium Amalgam.—This amalgam was prepared by treating 500 grams of sodium amalgam, at 85°, for periods of 2 minutes, with 4 separate portions, of 25 cc. each, of saturated strontium chloride solution. The amalgam was then washed, and shaken for 2 minutes with hot water. Analysis:

50 grams of the amalgam gave 0.1418 gram Na_2SO_4.

The remainder of the amalgam was, therefore, allowed to stand for 3 hours, with frequent shaking, under 300 cc. of a saturated solution of strontium chloride, containing a little strontium hydroxide. Analysis:

61 grams of the resulting amalgam gave 2.6326 grams $SrSO_4$ and 0.0180 gram Na_2SO_4.

Of this amalgam 391 grams were diluted with 425 grams of mercury, so that the product contained 0.987 per cent of strontium and 0.005 per cent of sodium.

Strontium amalgam should be kept in a small, tightly stoppered bottle. Although only slowly acted upon by water, it is very rapidly decomposed by the air.

Calcium Amalgam.—This amalgam was prepared by the electrolysis, in a beaker, of a saturated solution of pure calcium acetate. The cathode was a kilogram of mercury;

it was connected with the negative pole of the storage circuit by means of a platinum wire, surrounded by a glass tube, into which it was fused. The anode was a horizontally disposed piece of platinum foil. Current 14 volts and 3–4 amperes. During the electrolysis the mercury was frequently stirred with a glass rod. At the end of the operation, which lasted about 30 minutes, the solution was decanted and the surface of the amalgam washed once by decantation. The amalgam was further washed by pouring it through 3 portions of about 200 cc. of water, from one beaker to another, the wash-water being decanted each time. It was, finally, dried with filter paper and bottled. This amalgam was used within 1 hour of its preparation. Analysis:

100 grams of the amalgam gave 0.0423 gram CaO.

It therefore contained 0.0302 per cent of calcium.

Calcium amalgam is more rapidly acted upon by water than either barium or strontium amalgam, and it is exceedingly unstable in the presence of air.

The analyses given above were performed immediately after the preparation of the amalgams. Most of the amalgams did not remain homogeneous; they separated into a liquid and a crystalline portion and in taking out samples no effort was made to have their composition correspond with that of the amalgams as a whole. Unless otherwise stated, the amalgams used in the following experiments were the same as those mentioned above.

With but few exceptions, the salts used in the preparation of the solutions employed were obtained from Kahlbaum. Those which were not of his manufacture were of the chemically pure variety, and came through Eimer and Amend.

METHOD OF WORK.

In the experiments to be described below, except where otherwise stated, the following was the method of procedure: The amalgam and the solution in question were brought together in a 250 cc. beaker. Four other similar beakers were taken, each containing about 100 cc. of distilled water. After the amalgam and solution had been allowed to act the required length of time, during which the beaker containing them was frequently agitated, the solution was decanted and the amalgam immediately washed once by decantation. It was then poured into beaker No. 2, containing distilled water. This beaker was quickly shaken, the wash-water decanted, and the same operation repeated until the amalgam eventually reached beaker No. 5. The water in this beaker was also decanted and the amalgam was finally decomposed in it with dilute hydrochloric acid. The acid extracts were analyzed according to methods given in Treadwell's Quantitative Analysis.

The method of washing described above is very thorough and, with practice, the entire operation can be carried out in about 1 minute. The composition of the amalgams is not seriously affected during the washing.

I. POTASSIUM AND SODIUM.

The Action of Potassium Amalgam on Sodium Chloride Solution, and of Sodium Amalgam on Potassium Chloride Solution.—Approximately equimolecular liquid potassium and sodium amalgams were prepared by the addition of 2.5 grams of potassium and 1.5 grams of sodium, respectively, to 500 grams of mercury; and solutions of the chlorides of the 2 metals were made by dissolving 29.2 grams of sodium chloride and 37.2 grams of potassium chloride, each in 100 cc. of water. The following experiments were performed:

(1) Fifty grams of potassium amalgam were treated for 15 minutes, at 28°, with 50 cc. of sodium chloride solution. Hydrogen was very slowly evolved.

The resulting amalgam gave on analysis $KCl + NaCl = 0.2705$ gram; $K_2PtCl_6 = 0.0329$ gram.

That is, it contained 0.0053 gram potassium and 0.1026 gram sodium; in atoms $K:Na = 2.95:97.05$.

(2) Fifty grams of sodium amalgam were treated for 15 minutes, at 27°, with 50 cc. of potassium chloride solution. The evolution of hydrogen was very slow.

The resulting amalgam gave, on analysis, $KCl + NaCl = 0.2927$ gram; $K_2PtCl_6 = 0.9003$ gram.

That is, it contained 0.0064 gram sodium and 0.1451 gram potassium; in atoms, Na:K = 6.95:93.05.

(3) *The Preparation of Potassium Amalgam from Sodium Amalgam.*—Two hundred grams of sodium amalgam were treated with 5 separate portions, of 50 cc. each, of saturated potassium hydroxide solution. Upon shaking, after the addition of the first portion, the amalgam, which at first was pasty, solidified throughout, and the temperature rose from 23° to 26°. There was no perceptible evolution of hydrogen. In order to facilitate the removal of the sodium, the mixture was heated on the water-bath and the flask containing it was frequently shaken. Upon the application of heat, the amalgam melted and hydrogen was very feebly evolved. Before the addition of each fresh portion of the solution, the amalgam was quickly washed with cold water and, until the last treatment, it solidified each time so that the flask could be inverted without loss. At the end of the last heating the amalgam was pasty when cold. The entire operation lasted 2.5 hours. Analysis:

57 grams of the amalgam gave KCl + NaCl = 1.0797 grams.

This was dissolved in cold water and the solution made up to 250 cc. One-fifth of this volume gave 0.7028 gram K_2PtCl_6.

The amalgam, therefore, contained 0.989 per cent of potassium and 0.004 per cent of sodium.

(4) *The Preparation of Sodium Amalgam from Potassium Amalgam.*—One hundred grams of the amalgam, whose analysis has just been given, were treated, in the cold, with 5 successive portions, of 50 cc. each, of saturated sodium hydroxide solution. On shaking, after the addition of the first portion, the temperature fell from 23° to 21°. Hydrogen was very slowly evolved, and the amalgam became more liquid. Each portion of the solution was allowed to act for 30 minutes, and during the last half hour the mixture was heated on the water-bath. Analysis:

53 grams of the amalgam gave KCl + NaCl = 0.7154 gram; K_2PtCl_6 = none.

The amalgam, therefore, contained 0.532 per cent of sodium.

The Action of Potassium, Sodium and Lithium Amalgams on a Solution Containing Equimolecular Quantities of Sodium and Potassium Chlorides.—The amalgams used in these experiments were liquid, and the first 2 were approximately equimolecular; they consisted of a solution of 2.5 grams of potassium and of 1.5 grams of sodium, each in 500 grams of mercury. The solution employed was made by dissolving a mixture of 29.2 grams of sodium chloride and 37.2 grams of potassium chloride in water and diluting the solution to 250 cc.

(5) Fifty grams of potassium amalgam were treated for 30 minutes with 50 cc. of the solution mentioned. The evolution of hydrogen was very feeble, and the temperature remained constant at 25°.

The resulting amalgam gave, on analysis, $KCl + NaCl = 0.2967$ gram; $K_2PtCl_6 = 0.2820$ gram.

That is, it contained 0.0452 gram potassium and 0.0829 gram sodium; in atoms, $K : Na = 24.30 : 75.70$.

(6) Fifty grams of sodium amalgam were treated for 30 minutes with 50 cc. of the same solution. The evolution of hydrogen was very feeble and the temperature remained constant at 24°.5.

The resulting amalgam gave, on analysis, $KCl + NaCl = 0.2616$ gram; $K_2PtCl_6 = 0.2352$ gram.

That is, it contained 0.0377 gram potassium and 0.0746 gram sodium; in atoms, $K : Na = 22.93 : 77.07$.

(7) Fifty grams of lithium amalgam were treated for 30 minutes, at 17°, with 50 cc. of the same solution. The evolution of hydrogen in this case was also very feeble.

The resulting amalgam gave, on analysis, $KCl + NaCl = 0.0599$ gram; $K_2PtCl_6 = 0.0540$ gram.

That is, it contained 0.0087 gram potassium and 0.0171 gram sodium; in atoms, $K : Na = 23.05 : 76.95$.

The alcoholic filtrate from the potassium chlorplatinate was evaporated to dryness and the residue tested spectroscopically for lithium. None of that metal was present.

II. POTASSIUM AND LITHIUM.

(8) *The Action of Potassium Amalgam on Lithium Chloride Solution.*—Fifty grams of potassium amalgam were treated

for 30 minutes, at 33°, with 25 cc. of a solution containing 12.5 grams of lithium chloride. The evolution of hydrogen was more rapid than that produced by the action of the same amalgam on water.

The resulting amalgam gave, on analysis, $KCl + LiCl = 0.5867$ gram; $K_2PtCl_6 = 0.9354$ gram.

That is, it contained 0.1500 gram potassium and 0.0498 gram lithium; in atoms, $K:Li = 35.11:64.88$.

(9) *The Action of Lithium Amalgam on Potassium Chloride Solution.*—Forty grams of lithium amalgam were treated for 30 minutes with 50 cc. of a saturated solution of potassium chloride. The evolution of hydrogen was exceedingly feeble and the temperature remained constant at 19°.

The resulting amalgam gave, on analysis, $KCl + LiCl = 0.1708$ gram; Li_2SO_4 = none.

It, therefore, contained 0.0896 gram potassium, equivalent to 0.0161 gram lithium.

III. POTASSIUM AND BARIUM.

(10) *The Action of Potassium Amalgam on Barium Chloride Solution.*—Fifty grams of a liquid amalgam, made from 2.5 grams of potassium and 500 grams of mercury, were treated for 10 minutes with 50 cc. of a solution made by diluting saturated barium chloride solution with an equal volume of water. An exceedingly feeble evolution of hydrogen took place and the temperature rose from 22°.7 to 23°.1.

The resulting amalgam gave, on analysis, $BaSO_4 = 0.5824$ gram; K_2SO_4 = none.

It contained, therefore, 0.3427 gram barium, equivalent to 0.1953 gram potassium.

(11) *The Action of Barium Amalgam on Potassium Chloride Solution.*—Fifty grams of barium amalgam, prepared by the electrolysis of a solution of barium chloride with a mercury cathode (cf. calcium amalgam), were treated for 1 hour, at 23°, with 50 cc. of a saturated solution of potassium chloride. The evolution of hydrogen was moderately rapid.

The resulting amalgam gave, on analysis, $BaSO_4 = 0.5710$ gram; $K_2SO_4 = 0.0007$ gram.

That is, it contained 0.3360 gram barium and 0.0003 gram potassium; in atoms, Ba:K = 99.67:2(0.32).

The K_2SO_4 residue weighed 0.0012 gram and, viewed through a blue glass, it gave a good potassium flame. A blank experiment, performed at the same time, gave a residue which weighed 0.0005 gram.

(12) *The Action of Barium Amalgam on Potassium Sulphate Solution.*—Fifty grams of electrolytic barium amalgam (Exp. 11) were treated for 1 hour, at 23°, with 50 cc. of a saturated solution of potassium sulphate. The evolution of hydrogen was exceedingly feeble and the liquid became moderately turbid with barium sulphate.

The resulting amalgam gave, on analysis, $BaSO_4$ = 0.6713 gram; K_2SO_4 = 0.0103 gram.

That is, it contained 0.3950 gram barium and 0.0046 gram potassium; in atoms, Ba:K = 96.05:2(3.94).

The potassium sulphate residue in this case weighed 0.0108 gram. It gave a good potassium flame, and with chlorplatinic acid and alcohol a precipitate of potassium chlorplatinate.

(13) *The Action of Barium Amalgam on Potassium Carbonate Solution.*—Forty grams of barium amalgam were treated for 1 hour, at 25°, with 50 cc. of a 50 per cent potassium carbonate solution. No perceptible evolution of hydrogen took place, but the solution clouded up rapidly, owing to the formation of barium carbonate.

The resulting amalgam gave, on analysis, $BaSO_4$ = 0.0031 gram; K_2SO_4 = 0.1195 gram.

That is, it contained 0.0018 gram barium and 0.0536 gram potassium; in atoms, Ba:K = 1.88:2(98.12).

(14) *The Action of Barium Amalgam on Potassium Hydroxide Solution.*—Twenty-eight grams of barium amalgam were treated for 1 hour, at 23°, with 25 cc. of a saturated solution of potassium hydroxide. There was no perceptible evolution of hydrogen, but barium hydroxide separated in solid flakes. The barium hydroxide formed in the solution gave 0.2038 gram barium sulphate, equivalent to 0.0684 gram potassium.

The resulting amalgam gave, on analysis, $BaSO_4$ = 0.1589 gram; K_2PtCl_6 = 0.4104 gram.

That is, it contained 0.0935 gram barium and 0.0661 gram potassium; in atoms, Ba: K = 44.63: 2(55.37).

IV. POTASSIUM AND STRONTIUM.

(15) *The Action of Potassium Amalgam on Strontium Chloride Solution.*—Fifty grams of potassium amalgam were treated for 15 minutes, at 21°, with a solution of 15 grams of crystallized strontium chloride in 50 cc. of water. The evolution of hydrogen was moderate.

The resulting amalgam gave, on analysis, $SrSO_4$ = 0.8141 gram; K_2SO_4 = 0.0359 gram.

That is, it contained 0.0161 gram potassium and 0.3883 gram strontium; in atoms, K: Sr = 4.43: ½(95.57).

(16) *The Action of Strontium Amalgam on Potassium Chloride Solution.*—Forty grams of strontium amalgam were treated, for 30 minutes, at 23°, with 50 cc. of a saturated solution of potassium chloride. A very feeble evolution of hydrogen took place.

The resulting amalgam gave, on analysis, $SrSO_4$ = 0.2960 gram; K_2SO_4 = 0.1105 gram.

That is, it contained 0.1412 gram strontium and 0.0496 gram potassium; in atoms, Sr: K = 71.81: 2(28.21).

(17) *The Action of Strontium Amalgam on Potassium Sulphate Solution.*—Forty grams of strontium amalgam were treated, for 1 hour, at 25°, with 50 cc. of a saturated solution of potassium sulphate. There was practically no evolution of hydrogen, but the solution rapidly clouded up, owing to the formation of strontium sulphate.

The resulting amalgam gave, on analysis, $SrSO_4$ = 0.6116 gram; K_2SO_4 = 0.1053 gram.

That is, it contained 0.2917 gram strontium and 0.0473 gram potassium; in atoms, Sr:K=84.65:2(15.35).

(18) *The Action of Strontium Amalgam on Potassim Carbonate Solution.*—Forty grams of strontium amalgam were treated for 1 hour with 50 cc. of a 50 per cent potassium carbonate solution. There was a very feeble evolution of hydrogen, the solution rapidly became cloudy, owing to the forma-

tion of strontium carbonate, and the temperature rose slowly from 22° to 24°.

The resulting amalgam gave, on analysis, $SrSO_4$ = 0.0977 gram; K_2SO_4 = 0.5919 gram.

That is, it contained 0.0466 gram strontium and 0.2658 gram potassium; in atoms, Sr: K = 13.55: 2(86.45).

(19) *The Action of Strontium Amalgam on Potassium Hydroxide Solution.*—Fifty grams of strontium amalgam were treated for 15 minutes with 50 cc. of saturated potassium hydroxide solution. The evolution of hydrogen was imperceptible and the temperature rose from 25° to 27°. Solid strontium hydroxide separated in quantity.

The resulting amalgam gave, on analysis, $SrSO_4$ = 0.5131 gram; K_2SO_4 = 0.5774 gram.

That is, it contained 0.2447 gram strontium and 0.2593 gram potassium; in atoms, Sr: K = 45.75: 2(54.25).

V. POTASSIUM AND CALCIUM.

(20) *The Action of Potassium Amalgam on Calcium Chloride Solution.*—Fifty grams of potassium amalgam were treated for 15 minutes, at the ordinary temperature, with 20 cc. of a 50 per cent calcium chloride solution. The evolution of hydrogen was much more rapid than that which the same amalgam gave with water; the surface of the amalgam became covered in spots with a dark deposit, and later the solution became gray and turbid, owing to the presence of very finely divided mercury.

The resulting amalgam gave, on analysis, CaO = 0.0830 gram; K_2SO_4 = 0.7758 gram.

That is, it contained 0.3484 gram potassium and 0.0593 gram calcium; in atoms, K: Ca = 75.01: $\frac{1}{2}$(24.99).

(21) *The Action of Calcium Amalgam on Potassium Chloride Solution.*—One hundred grams of calcium amalgam were treated for 30 minutes, at 20°, with 50 cc. of a saturated solution of potassium chloride. The evolution of hydrogen was very feeble.

The resulting amalgam gave, on analysis, CaO = 0.0230 gram; K_2SO_4 = 0.0348 gram.

That is, it contained 0.0164 gram calcium and 0.0156 gram potassium; in atoms, Ca : K = 50.66 : 2(49.33).

(22) *The Action of Calcium Amalgam on Potassium Hydroxide Solution.*—Fifty grams of calcium amalgam were treated for 30 minutes, at the ordinary temperature, with 50 cc. of a saturated solution of potassium hydroxide. There was no perceptible evolution of hydrogen, but calcium hydroxide separated in solid form at the surface of the amalgam. The potassium hydroxide mother liquor gave 0.0254 gram calcium oxide, equivalent to 0.0354 gram potassium.

The resulting amalgam gave, on analysis, $CaO = 0.0110$ gram; $K_2SO_4 = 0.0728$ gram.

That is, it contained 0.0078 gram calcium and 0.0327 gram potassium; in atoms, Ca : K = 31.78 : 2(68.22).

VI. POTASSIUM AND MAGNESIUM.

(23) *The Action of Potassium Amalgam on Magnesium Sulphate Solution.*—Fifty grams of potassium amalgam were treated for 10 minutes, at 24°, with 25 cc. of a saturated solution of magnesium sulphate. The evolution of hydrogen was more rapid than that which the same amalgam gave with water.

The resulting amalgam gave, on analysis, $K_2SO_4 + MgSO_4 = 0.8730$ gram; $Mg_2P_2O_7 = 0.0089$ gram.

That is, it contained 0.3878 gram potassium and 0.0019 gram magnesium; in atoms, K : Mg = 98.45 : $\frac{1}{2}$(1.55).

(24) *The Action of Magnesium Amalgam on Potassium Hydroxide Solution.*—To 200 grams of mercury in a 250 cc. beaker, 1 gram of bright magnesium ribbon was added, in short pieces. In order to bring about amalgamation, the metals were just covered with water and a little very dilute hydrochloric acid was added. Then, after having stirred the mixture, a solution of 70 grams of potassium hydroxide in 50 cc. of water was added. The temperature was 35°. The strips of magnesium were pressed down on the mercury with a glass rod from time to time during the action, which was allowed to continue for 1 hour. There was a moderate evolution of hydrogen, especially from the pieces of magnesium which were

in contact with the mercury, and these were considerably corroded, though bright, at the end of the action. In washing the amalgam, the liquid metal was readily poured away from the strips of magnesium.

The resulting amalgam gave, on analysis, $MgSO_4 + K_2SO_4 =$ 0.4407 gram; $MgNH_4PO_4 =$ none.

It, therefore, contained 0.1979 gram potassium, equivalent to 0.0616 gram magnesium.

VII. SODIUM AND LITHIUM.

(25) *The Action of Sodium Amalgam on Lithium Chloride Solution.*—Fifty grams of sodium amalgam were treated for 30 minutes, at 35°, with 25 cc. of a solution containing 12.5 grams of lithium chloride. The evolution of hydrogen, which was slow at first, became more and more rapid, until it approached in rapidity that produced by the action of potassium amalgam on the same solution (Exp. 8).

The resulting amalgam gave, on analysis, $NaCl + LiCl =$ 1.1570 grams; $Li_2SO_4 =$ 0.0352 gram.

That is, it contained 0.4451 gram sodium and 0.0045 gram lithium; in atoms, Na: Li = 96.79: 3.21.

(26) *The Action of Lithium Amalgam on Sodium Chloride Solution.*—Forty grams of lithium amalgam were treated for 30 minutes, at 18°, with 50 cc. of a saturated solution of sodium chloride. The evolution of hydrogen was exceedingly feeble.

The resulting amalgam gave, on analysis, $NaCl + LiCl =$ 0.0948 gram; $Li_2SO_4 =$ none.

It, therefore, contained 0.0373 gram sodium, equivalent to 0.0114 gram lithium.

VIII. SODIUM AND BARIUM.

(27) *The Action of Sodium Amalgam on Barium Chloride Solution.*—Fifty grams of a liquid amalgam, made by the addition of 1.5 grams of sodium to 500 grams of mercury, were treated, for 10 minutes, with 50 cc. of a solution made by diluting saturated barium chloride solution with an equal volume of water. An exceedingly feeble evolution of hydrogen took place and the temperature rose from 22°.5 to 23°.

The resulting amalgam gave, on analysis, $BaSO_4$ = 0.5293 gram; Na_2SO_4 = none.

It, therefore, contained 0.3114 gram barium, equivalent to 0.1304 gram sodium.

(28) *The Action of Barium Amalgam on Sodium Chloride Solution.*—Fifty grams of electrolytic barium amalgam (Exp. 11) were treated for 1 hour, at 23°, with 50 cc. of a saturated solution of sodium chloride. The evolution of hydrogen was very slow.

The resulting amalgam gave, on analysis, $BaSO_4$ = 1.0499 grams; Na_2SO_4 = 0.0021 gram.

That is, it contained 0.6178 gram barium and 0.0007 gram sodium; in atoms, Ba : Na = 99.35 : 2(0.65).

(29) *The Action of Barium Amalgam on Sodium Sulphate Solution.*—Fifty grams of electrolyic barium amalgam (Exp. 11) were treated for 1 hour, at 23°, with 50 cc. of a saturated solution of sodium sulphate. The evolution of hydrogen was very feeble, but faster than that which the same amalgam gave with potassium sulphate solution (Exp. 12). Also more barium sulphate was formed in the aqueous liquid.

The resulting amalgam gave, on analysis, $BaSO_4$ = 0.6838 gram; Na_2SO_4 = 0.0029 gram.

That is, it contained 0.4024 gram barium and 0.0009 gram sodium; in atoms, Ba : Na = 98.63 : 2(1.37)

(30) *The Action of Barium Amalgam on Sodium Carbonate Solution.*—Forty grams of barium amalgam were treated for 1 hour, at 24°, with 50 cc. of a solution of 20 grams of anhydrous sodium carbonate in 100 cc. of water. There was no perceptible evolution of hydrogen, but the solution became clouded with barium carbonate.

The resulting amalgam gave, on analysis, $BaSO_4$ = 0.1183 gram; Na_2SO_4 = 0.0290 gram.

That is, it contained 0.0696 gram barium and 0.0094 gram sodium; in atoms, Ba : Na = 71.29 : 2(28.71).

(31) *The Action of Barium Amalgam on Sodium Hydroxide Solution.*—Sixty grams of barium amalgam were treated for 65 minutes, at 45°, with 100 cc. of a saturated solution of sodium

hydroxide. There was no perceptible evolution of hydrogen, but barium hydroxide separated in quantity.

The resulting amalgam gave, on analysis, $BaSO_4$ = 0.0415 gram; Na_2SO_4 = 0.1868 gram.

That is, it contained 0.0244 gram barium and 0.0606 gram sodium; in atoms, Ba : Na = 11.91 : 2(88.09).

IX. SODIUM AND STRONTIUM.

(32) *The Action of Sodium Amalgam on Strontium Chloride Solution.*—Fifty grams of sodium amalgam were treated for 25 minutes, at 18°, with a solution of 15 grams of crystalline strontium chloride in 50 cc. of water. A moderately rapid evolution of hydrogen took place.

The resulting amalgam gave, on analysis, $SrSO_4$ = 1.6891 grams; $NaSO_4$ = 0.5906 gram.

That is, it contained 0.1915 gram sodium and 0.8057 gram strontium; in atoms, Na : Sr = 31.11 : ½(68.89).

(33) *The Action of Strontium Amalgam on Sodium Chloride Solution.*—Forty grams of strontium amalgam were treated for 30 minutes, at 25°, with 50 cc. of a saturated sodium chloride solution. The evolution of hydrogen was moderate.

The resulting amalgam gave, on analysis, $SrSO_4$ = 0.2337 gram; Na_2SO_4 = 0.0755 gram.

That is, it contained 0.1115 gram strontium and 0.0245 gram sodium; in atoms, Sr : Na = 70.55 : 2(29.45).

(34) *The Action of Strontium Amalgam on Sodium Sulphate Solution.*—Forty grams of strontium amalgam were treated, for 1 hour, with 50 cc. of a saturated solution of sodium sulphate. The evolution of hydrogen was practically imperceptible, the temperature remained constant at 26°, and the solution rapidly clouded up, owing to the formation of strontium sulphate.

The resulting amalgam gave, on analysis, $SrSO_4$ = 0.0693 gram; Na_2SO_4 = 0.4541 gram.

That is, it contained 0.0331 gram strontium and 0.1473 gram sodium; in atoms, Sr : Na = 10.57 : 2(89.43).

(35) *The Action of Strontium Amalgam on Sodium Carbonate Solution.*—Forty grams of strontium amalgam were

treated for 1 hour, at 22°, with 50 cc. of a solution of 20 grams of anhydrous sodium carbonate in 100 cc. of water. The evolution of hydrogen was very feeble and the solution became turbid, owing to the formation of strontium carbonate.

The resulting amalgam gave, on analysis, $SrSO_4$ = 0.4201 gram; Na_2SO_4 = 0.1998 gram.

That is, it contained 0.2004 gram strontium and 0.0648 gram sodium; in atoms, Sr : Na = 61.94 : 2(38.06).

(36) *The Action of Strontium Amalgam on Sodium Hydroxide Solution.*—Fifty grams of strontium amalgam were treated, for 15 minutes, with 50 cc. of a saturated solution of sodium hydroxide. There was no perceptible evolution of hydrogen. The temperature rose from 25° to 26°.5, and solid flakes of strontium hydroxide separated at the surface of the amalgam.

The resulting amalgam gave, on analysis, $SrSO_4$ = 0.2092 gram; Na_2SO_4 = 0.6263 gram.

That is, it contained 0.0998 gram strontium and 0.2031 gram soidum; in atoms, Sr : Na = 20.54 : 2(79.46).

X. SODIUM AND CALCIUM.

(37) *The Action of Sodium Amalgam on Calcium Chloride Solution.*—Fifty grams of sodium amalgam were treated, for 15 minutes, at the ordinary temperature, with 20 cc. of a 50 per cent solution of calcium chloride. A moderately rapid evolution of hydrogen took place, but the solution did not become turbid with finely divided mercury as it did when acted upon by potassium amalgam (Exp. 20).

The resulting amalgam gave, on analysis, CaO = 0.0216 gram; Na_2SO_4 = 1.6117 grams.

That is, it contained 0.5226 gram sodium and 0.0154 gram calcium; in atoms, Na : Ca = 96.72 : ½(3.28).

(38) *The Action of Calcium Amalgam on Sodium Chloride Solution.*—One hundred grams of calcium amalgam were treated for 30 minutes, at 20°, with 50 cc. of a saturated solution of sodium chloride. The evolution of hydrogen was very feeble.

The resulting amalgam gave, on analysis, CaO = 0.0157 gram; Na_2SO_4 = 0.0569 gram.

That is, it contained 0.0112 gram calcium and 0.0184 gram sodium; in atoms, Ca: Na = 25.90: 2(74.09).

(39) *The Action of Calcium Amalgam on Sodium Hydroxide Solution.*—Sixty grams of calcium amalgam were treated for 30 minutes, at the ordinary temperature, with 50 cc. of a saturated solution of sodium hydroxide. There was no perceptible evolution of hydrogen, but calcium hydroxide separated in solid form. The sodium hydroxide mother liquor contained 0.0342 gram calcium oxide, equivalent to 0.0280 gram sodium.

The resulting amalgam gave, on analysis, CaO = 0.0015 gram; Na_2SO_4 = 0.0787 gram.

This is equivalent to 0.0011 gram calcium and 0.0255 gram sodium; in atoms, Ca: Na = 4.72: 2(95.27).

XI. SODIUM AND MAGNESIUM.

(40) *The Action of Sodium Amalgam on Magnesium Sulphate Solution.*—Fifty grams of sodium amalgam were treated for 10 minutes, at 24°, with 25 cc. of a saturated solution of magnesium sulphate. The evolution of hydrogen was more rapid than that which the same amalgam gave with water.

The resulting amalgam gave, on analysis, $Na_2SO_4 + MgSO_4$ = 1.6396 grams; $Mg_2P_2O_7$ = 0.0069 gram.

That is, it contained 0.5293 gram sodium and 0.0015 gram magnesium; in atoms, Na: Mg = 99.47: ½(0.53).

(41) *The Action of Magnesium Amalgam on Sodium Hydroxide Solution.*—To 200 grams of mercury, in a 250 cc. beaker, 1 gram of bright magnesium ribbon was added, in short strips. The metals were then just covered with water and a little very dilute hydrochloric acid was added. After having stirred the mixture, a solution of 50 grams of sodium hydroxide, in 50 cc. of water, was added. The temperature was 39°. During the action, which was allowed to continue for 1 hour, the strips of magnesium were pressed down on the mercury from time to time with a glass rod. The evolution of hydrogen was much slower in this case than it was under the same conditions with potassium hydroxide solution (Exp. 24), and the strips of magnesium were also much less corroded at the end

of the action. In washing, the liquid amalgam was readily poured off from the strips of magnesium.

The resulting amalgam gave, on analysis, $MgSO_4 + Na_2SO_4 = 0.1235$ gram; $MgNH_4PO_4$ = none.

It, therefore, contained, 0.4000 gram sodium, equivalent to 0.0211 gram magnesium.

XII. LITHIUM AND BARIUM.

(42) *The Action of Lithium Amalgam on Barium Chloride Solution.*—Forty grams of lithium amalgam were treated for 10 minutes, at 26°, with 50 cc. of saturated barium chloride solution. The evolution of hydrogen was exceedingly feeble.

The resulting amalgam gave, on analysis, $BaSO_4 = 0.2920$ gram; Li_2SO_4 = none.

It, therefore, contained 0.1718 gram barium, equivalent to 0.0176 gram lithium.

(43) *The Action of Barium Amalgam on Lithium Chloride Solution.*—Fifty grams of barium amalgam were treated for 30 minutes, at 30°, with 25 cc. of a solution containing 12.5 grams of lithium chloride. The evolution of hydrogen was very slow.

The amalgam gave, on analysis, $BaSO_4 = 0.1491$ gram; Li_2SO_4 = none.

(44) *The Action of Barium Amalgam on Lithium Sulphate Solution.*—Fifty grams of barium amalgam were treated for 30 minutes, at 25°, with 25 cc. of a solution containing 6 grams of crystalline lithium sulphate. The evolution of hydrogen was very slow and very little barium sulphate was formed.

The amalgam gave, on analysis, $BaSO_4 = 0.1777$ gram; Li_2SO_4 = none.

(45) *The Action of Barium Amalgam on Lithium Hydroxide Solution.*—Fifty grams of barium amalgam were treated for 30 minutes, at 24°, with 50 cc. of saturated lithium hydroxide solution. The evolution of hydrogen was barely perceptible.

The amalgam gave, on analysis, $BaSO_4 = 0.1454$ gram; Li_2SO_4 = none.

(46) *The Action of Barium Amalgam on a Mixed Lithium Chloride, Hydroxide and Sulphate Solution.*—Fifty grams of

electrolytic barium amalgam (Exp. 11) were treated for 1 hour, at 23°, with 50 cc. of a solution made by dissolving 15 grams of lithium chloride and 2 grams of crystalline lithium sulphate in a mixture of 25 cc. of saturated lithium hydroxide solution and 75 cc. of water. An exceedingly feeble evolution of hydrogen took place and the solution became slightly turbid.

The amalgam gave, on analysis, $BaSO_4$ = 0.7079 gram; Li_2SO_4 = none.

XIII. LITHIUM AND STRONTIUM.

(47) *The Action of Lithium Amalgam on Strontium Chloride Solution.*—Forty grams of lithium amalgam were treated for 15 minutes, at 26°, with a solution of 15 grams of crystalline strontium chloride in 50 cc. of water. A very feeble evolution of hydrogen took place.

The resulting amalgam gave, on analysis, $SrSO_4$ = 0.2155 gram; Li_2SO_4 = none.

It, therefore, contained 0.1028 gram strontium, equivalent to 0.0165 gram lithium.

(48) *The Action of Strontium Amalgam on Lithium Chloride Solution.*—Fifty grams of strontium amalgam, made by the electrolysis of a solution of strontium chloride with a mercury cathode, were treated for 1 hour, at 23°, with 50 cc. of a solution containing 25 grams of lithium chloride. The evolution of hydrogen was moderately rapid.

The resulting amalgam gave, on analysis, $SrSO_4$ = 0.2545 gram; Li_2SO_4 = 0.0013 gram.

That is, it contained 0.1214 gram strontium and 0.00016 gram lithium; in atoms, Sr : Li = 98.32 : 2(1.67).

The lithium sulphate residue gave the spectroscopic test for lithium.

(49) *The Action of Strontium Amalgam on Lithium Sulphate Solution.*—Fifty grams of electrolytic strontium amalgam (Exp. 48) were treated for 1 hour, at 23°, with a solution of 10 grams of crystalline lithium sulphate, in 40 cc. of water. The evolution of hydrogen was moderately rapid and strontium sulphate was formed in large quantity.

The resulting amalgam gave, on analysis, $SrSO_4$ = 0.4988 gram; Li_2SO_4 = 0.0037 gram.

That is, it contained 0.2379 gram strontium and 0.00047 gram lithium; in atoms, Sr: Li = 97.58: 2(2.41).

The lithium sulphate residue gave a very bright and persistent lithium spectrum.

(50) *The Action of Strontium Amalgam on Lithium Hydroxide Solution.*—Fifty grams of electrolytic strontium amalgam (Exp. 48) were treated for 1 hour, at 22°, with 25 cc. of a saturated solution of lithium hydroxide. The evolution of hydrogen was very feeble.

The resulting amalgam gave, on analysis, $SrSO_4$ = 1.2509 grams; Li_2SO_4 = 0.0087 gram.

That is, it contained 0.5980 gram strontium and 0.0011 gram lithium; in atoms, Sr: Li = 97.74: 2(2.26).

The lithium sulphate residue gave an especially bright and persistent lithium spectrum.

XIV. LITHIUM AND CALCIUM.

(51) *The Action of Lithium Amalgam on Calcium Chloride Solution.*—Thirty-five grams of lithium amalgam were treated for 15 minutes, at 24°, with 50 cc. of a 50 per cent calcium chloride solution. The evolution of hydrogen was rapid at first, but it gradually slowed down.

The resulting amalgam gave, on analysis, CaO = 0.0270 gram; Li_2SO_4 = none.

It, therefore, contained 0.0193 gram calcium, equivalent to 0.0067 gram lithium.

(52) *The Action of Calcium Amalgam on Lithium Chloride Solution.*—One hundred grams of calcium amalgam were treated for 30 minutes, at 20°, with 50 cc. of a solution containing 37.5 grams of lithium chloride. The evolution of hydrogen was slow.

The resulting amalgam gave, on analysis, CaO = 0.0320 gram; Li_2SO_4 = 0.0033 gram.

That is, it contained 0.0229 gram calcium and 0.00042 gram lithium; in atoms, Ca: Li = 90.49: 2(9.50).

The lithium sulphate residue gave a good lithium spectrum.

(53) *The Action of Calcium Amalgam on Lithium Hydroxide Solution.*—One hundred grams of calcium amalgam were treated for 30 minutes, at 20°, with 50 cc. of a saturated solution of lithium hydroxide. The evolution of hydrogen was very slow.

The resulting amalgam gave, on analysis, $CaO = 0.0290$ gram; $Li_2SO_4 = 0.0114$ gram.

That is, it contained 0.0207 gram calcium and 0.0014 gram lithium; in atoms, $Ca:Li = 71.40:2(28.60)$.

The lithium sulphate residue gave a bright and very persistent lithium spectrum.

XV. LITHIUM AND MAGNESIUM.

(54) *The Action of Lithium Amalgam on Magnesium Sulphate Solution.*—Forty grams of lithium amalgam were treated for 10 minutes, at 22°, with 25 cc. of a saturated solution of magnesium sulphate. The evolution of hydrogen was at first very rapid, but it quickly slowed down.

On analysis, the mercury was found to contain neither lithium nor magnesium.

(55) *The Action of Magnesium Amalgam on a Mixed Lithium Chloride and Hydroxide Solution.*—To 200 grams of mercury, in a 250 cc. beaker, 0.5 gram of bright magnesium ribbon was added, in short strips. The surface of the metals was just covered with water and then 1 cc. of 3 per cent hydrochloric acid was added. After having stirred the mixture, a solution of 15 grams of lithium chloride, in a mixture of 10 cc. of saturated lithium hydroxide solution and 25 cc. of water, was added. The temperature was 24°. The evolution of hydrogen was rapid and a very dark deposit of finely divided mercury was formed which soon rendered the solution dark and opaque. The action was allowed to continue for 1 hour.

The resulting amalgam gave, on analysis, $Li_2SO_4 = 0.0486$ gram.

It, therefore, contained 0.0062 gram lithium, equivalent to 0.0105 gram magnesium.

XVI. BARIUM AND STRONTIUM.

(56) *The Action of Barium Amalgam on Strontium Chloride Solution.*—Fifty grams of electrolytic barium amalgam (Exp. 11) were treated for 1 hour, at 22°, with 50 cc. of a saturated solution of strontium chloride. The evolution of hydrogen was very feeble.

The amalgam gave, on analysis, $BaCrO_4$ = 0.5292 gram; $SrSO_4$ = none.

(57) *The Action of Strontium Amalgam on Barium Chloride Solution.*—Fifty grams of strontium amalgam were treated for 10 minutes, at 26°, with 50 cc. of a saturated solution of barium chloride. The evolution of hydrogen was slow.

The resulting amalgam gave, on analysis, $BaCrO_4$ = 0.9476 gram; $SrSO_4$ = 0.2466 gram.

That is, it contained 0.1176 gram strontium and 0.5136 gram barium; in atoms, Sr : Ba = 26.43 : 73.57.

XVII. BARIUM AND CALCIUM.

(58) *The Action of Barium Amalgam on Calcium Chloride Solution.*—Fifty grams of electrolytic barium amalgam (Exp. 11) were treated for 1 hour, at 19°, with 50 cc. of a saturated solution of calcium chloride. The evolution of hydrogen was at first very slow, but it gradually became more rapid; during the last 45 minutes it was moderate.

The resulting amalgam gave, on analysis, $BaCrO_4$ = 0.3820 gram; CaC_2O_4 = none.

(59) *The Action of Calcium Amalgam on Barium Chloride Solution.*—One hundred grams of calcium amalgam were treated for 30 minutes, at 20°, with 50 cc. of a saturated solution of barium chloride. The evolution of hydrogen was exceedingly slow.

The resulting amalgam gave, on analysis, CaO = 0.0219 gram; $BaSO_4$ = 0.0663 gram.

That is, it contained 0.0156 gram calcium and 0.0390 gram barium; in atoms, Ca : Ba = 57.89 : 42.11.

XVIII. BARIUM AND MAGNESIUM.

(60) *The Action of Barium Amalgam on Magnesium Sulphate Solution.*—Fifty grams of electrolytic barium amalgam

(Exp. 11) were treated for 1 hour, at 22°, with 50 cc. of a saturated solution of magnesium sulphate. The evolution of hydrogen was moderately rapid and about 0.1 gram of barium sulphate was formed in the solution.

The resulting amalgam gave, on analysis, $BaSO_4$ = 0.3476 gram; $Mg_2P_2O_7$ = 0.0022 gram.

It, therefore, contained 0.2045 gram barium and 0.00048 gram magnesium; in atoms, Ba : Mg = 98.69 : 1.31.

(61) *The Action of Magnesium Amalgam on Barium Chloride Solution.*—The surface of 200 grams of mercury, in a 150 cc. beaker, was just covered with water, and under this was introduced 0.2 gram of brightly polished magnesium ribbon, in short pieces. To the mixture 1 cc. of 3 per cent hydrochloric acid was added, and then, after a few seconds, 50 cc. of saturated barium chloride solution. After 20 minutes the solution was neutral to litmus and the evolution of hydrogen was still moderate. The temperature was 24°. The action was allowed to continue for 1 hour.

The resulting amalgam gave, on analysis, $BaSO_4$ = 0.2665 gram; $MgNH_4PO_4$ = none.

It, therefore, contained 0.1568 gram barium, equivalent to 0.0278 gram magnesium.

XIX. STRONTIUM AND CALCIUM.

(62) *The Action of Strontium Amalgam on Calcium Chloride Solution.*—Fifty grams of electrolytic strontium amalgam (Exp. 48) were treated for 15 minutes, at 20°, with 50 cc. of a saturated solution of calcium chloride. The evolution of hydrogen was rapid.

The resulting amalgam gave, on analysis, CaO = 0.0108 gram; $SrSO_4$ = 1.1160 grams.

That is, it contained 0.5323 gram strontium and 0.0077 gram calcium; in atoms, Sr : Ca = 96.93 : 3.07.

(63) *The Action of Calcium Amalgam on Strontium Chloride Solution.*—One hundred grams of calcium amalgam were treated for 30 minutes, at 20°, with 50 cc. of a saturated solution of strontium chloride. The evolution of hydrogen was

very slow; it was much faster, however, than that which the same amalgam gave with barium chloride solution (Exp. 59).

The resulting amalgam gave, on analysis, CaO = 0.0109 gram; $SrSO_4$ = 0.0892 gram.

That is, it contained 0.0078 gram calcium and 0.0425 gram strontium; in atoms, Ca : Sr = 28.57 : 71.42.

XX. STRONTIUM AND MAGNESIUM.

(64) *The Action of Strontium Amalgam on Magnesium Sulphate Solution.*—Fifty grams of electrolytic strontium amalgam (Exp. 48) were treated for 30 minutes, at 22°, with 50 cc. of a saturated solution of magnesium sulphate. The evolution of hydrogen was much faster than that given by the same solution with barium amalgam, and about 0.3 gram of strontium sulphate was formed in the solution (cf. Exp. 60).

The resulting amalgam gave, on analysis, $SrSO_4$ = 0.9679 gram; $Mg_2P_2O_7$ = 0.0031 gram.

That is, it contained 0.4616 gram strontium and 0.00068 gram magnesium; in atoms, Sr : Mg = 99.48 : 0.52.

(65) *The Action of Magnesium Amalgam on Strontium Chloride Solution.*—The surface of 200 grams of mercury, in a 150 cc. beaker, was just covered with water, and under this was introduced 0.2 gram of brightly polished magnesium ribbon, in short pieces. To the mixture 1 cc. of 3 per cent hydrochloric acid was added, and then, after a few seconds, 50 cc. of saturated strontium chloride solution. After 20 minutes the solution was neutral to litmus and the evolution of hydrogen was rapid. A dark deposit of finely divided mercury was formed, and this soon rendered the solution dark and turbid. The temperature was 23°. The action was allowed to continue for 1 hour.

The resulting amalgam gave, on analysis, $SrSO_4$ = 0.0068 gram; $MgNH_4PO_4$ = none.

It, therefore, contained 0.0032 gram strontium, equivalent to 0.0009 gram magnesium.

XXI. CALCIUM AND MAGNESIUM.

(66) *The Action of Calcium Amalgam on Magnesium Sulphate Solution.*—One hundred grams of calcium amalgam

were treated for 30 minutes, at 20°, with 50 cc. of a saturated solution of magnesium sulphate. The evolution of hydrogen was moderate and calcium sulphate was formed in the solution.

The resulting amalgam gave, on analysis, CaO = 0.0084 gram; $MgNH_4PO_4$ = none.

(67) *The Action of Magnesium Amalgam on Calcium Chloride Solution.*—Two hundred grams of mercury and 0.5 gram of bright magnesium ribbon were treated, as described in Experiments 61 and 65, with 50 cc. of a saturated solution of calcium chloride. After 30 minutes the solution was neutral to litmus. The temperature was 25° and the evolution of hydrogen was rapid. A very dark deposit of finely divided mercury, which soon rendered the solution opaque, was formed. The action was allowed to continue for 1 hour.

On analysis, neither calcium nor magnesium was found in the mercury.

TABULATION OF RESULTS.

In comparing the following results, allowance should be made for the differences in concentration of the various solutions employed. For example, the relative difference in the action of barium, or strontium amalgam on potassium and sodium carbonate solutions on the one hand, and on their hydroxide solutions on the other, can readily be accounted for on taking into consideration the relative concentrations of the carbonate solutions of these metals, and of their hydroxide solutions, respectively:

The atomic ratios in Experiments 49 and 50 are misleading. The amalgam used in the latter was much richer in strontium than that used in the former. More lithium, by weight, was displaced from the hydroxide solution than from either of the others. The same is true in Experiments 13 and 18; the barium amalgam used in Experiment 13 was liquid, and very dilute, while the strontium amalgam used in Experiment 18 was a mixture of liquid and solid amalgam and contained more than 1.5 per cent of strontium.

Amalgam.	Expt. No.	Solution.	Time.	Temperature.	Evolution of hydrogen.	Atomic proportions of the amalgamated metals.
Potassium	1	NaCl	15 min.	28°	very slow	K : Na = 2.95 : 97.05
	3	NaOH	2½ hours	water-bath	very feeble	0.99 per cent ~~K~~ Na
	5	KCl + NaCl	30 min.	25°	very feeble	K : Na = 24.30 : 75.70
	8	LiCl	30 min.	33°	moderate	K : Li = 35.11 : 64.88
	10	$BaCl_2$	10 min.	23°	very feeble	0.68 per cent Ba
	15	$SrCl_2$	15 min.	21°	moderate	K : Sr = 4.43 : ½(95.57)
	20	$CaCl_2$	15 min	room temp.	rapid	K : Ca = 75.01 : ½(24.99)
	23	$MgSO_4$	10 min.	24°	rapid	K : Mg = 98.45 : ½(1.55)
Sodium	2	KCl	15 min.	27°	very slow	Na : K = 6.95 : 93.05
	~~4~~ 3	KOH	2½ hours	water-bath	very feeble	0.53 per cent ~~Na~~ K
	6	KCl + NaCl	30 min.	24°.5	very feeble	K : Na = 22.93 : 77.07
	25	LiCl	30 min.	35°	moderate	Na : Li = 96.79 : 3.21
	27	$BaCl_2$	10 min.	23°	very feeble	0.62 per cent Ba
	32	$SrCl_2$	25 min.	18°	fairly rapid	Na : Sr = 31.11 : ½(68.89)
	37	$CaCl_2$	15 min.	room. temp.	fairly rapid	Na : Ca = 96.72 : ½(3.28)
	40	$MgSO_4$	10 min.	24°	fairly rapid	Na : Mg = 99.47 : ½(0.53)
Lithium	7	KCl + NaCl	30 min	17°	very feeble	K : Na = 23.05 : 76 : 95
	9	KCl	30 min	19°	very feeble	0.22 per cent K
	26	NaCl	30 min.	18°	very feeble	0.09 per cent Na
	42	$BaCl_2$	10 min.	26°	very feeble	0.43 per cent Ba
	47	$SrCl_2$	15 min.	26°	very feeble	0.25 per cent Sr
	51	$CaCl_2$	15 min.	24°	rapid	0.05 per cent Ca
	54	$MgSO_4$	10 min.	22°	very rapid	Pure mercury

Amalgam.	Expt. No.	Solution.	Time.	Temperature.	Evolution of hydrogen.	Atomic proportions of the amalgamated metals.
Barium	11	KCl	1 hour	23°	moderate	Ba : K = 99.67 : 2(0.32)
	12	K_2SO_4	1 hour	23°	very feeble	= 96.05 : 2(3.94)
	13	K_2CO_3	1 hour	25°	imperceptible	= 1.88 : 2(98.12)
	14	KOH	1 hour	23°	imperceptible	= 44.63 : 2(55.37)
	28	NaCl	1 hour	23°	very slow	Ba : Na = 99.35 : 2(0.65)
	29	Na_2SO_4	1 hour	23°	very slow	= 98.63 : 2(1.37)
	30	Na_2CO_3	1 hour	24°	imperceptible	= 71.29 : 2(28.71)
	31	NaOH	65 min.	45°	imperceptible	= 11.91 : 2(88.09)
	43	LiCl	30 min.	33°	very slow	0.17 per cent Ba
	44	Li_2SO_4	30 min.	25°	very slow	0.21 per cent Ba
	45	LiOH	30 min.	24°	very feeble	0.17 per cent Ba
	46	$Li(Cl,OH,\frac{1}{2}SO_4)$	1 hour	23°	very feeble	0.83 per cent Ba
	56	$SrCl_2$	1 hour	22°	very feeble	0.57 per cent Ba
	58	$CaCl_2$	1 hour	19°	moderate	0.41 per cent Ba
	60	$MgSO_4$	1 hour	22°	fairly rapid	Ba : Mg = 98.69 : 1.31
Strontium	16	KCl	30 min.	23°	very feeble	Sr : K = 71.81 : 2(28.21)
	17	K_2SO_4	1 hour	25°	imperceptible	= 84.65 : 2(15.35)
	18	K_2CO_3	1 hour	23°	very feeble	= 13.55 : 2(86.45)
	19	KOH	15 min.	26°	imperceptible	= 45.75 : 2(54.25)
	33	NaCl	30 min.	25°	moderate	Sr : Na = 70.55 : 2(29.45)
	34	Na_2SO_4	1 hour	26°	imperceptible	= 10.57 : 2(89.43)
	35	Na_2CO_3	1 hour	22°	very feeble	= 61.94 : 2(38.06)

Amalgam.	Expt. No.	Solution.	Time.	Temperature.	Evolution of hydrogen.	Atomic proportions of the amalgamated metals.
Strontium	36	$NaOH$	15 min.	26°	imperceptible	Sr:Na = 20.54:2(79.46)
	48	$LiCl$	1 hour	23°	fairly rapid	Sr:Li = 98.32:2(1.67)
	49	Li_2SO_4	1 hour	23°	fairly rapid	= 97.58:2(2.41)
	50	$LiOH$	1 hour	22°	very feeble	= 97.74:2(2.26)
	57	$BaCl_2$	10 min.	26°	slow	Sr:Ba = 26.43:73.57
	62	$CaCl_2$	15 min.	20°	rapid	Sr:Ca = 96.93:3.07
	64	$MgSO_4$	30 min.	22°	rapid	Sr:Mg = 99.48:0.52
Calcium	21	KCl	30 min.	20°	very feeble	Ca:K = 50.66:2(49.33).
	22	KOH	30 min.	room temp.	imperceptible	= 31.78:2(68.22)
	38	$NaCl$	30 min.	20°	very feeble	Ca:Na = 25.90:2(74.09)
	39	$NaOH$	30 min.	room temp.	imperceptible	= 4.72:2(95.27)
	52	$LiCl$	30 min.	20°	slow	Ca:Li = 90.49:2(9.50)
	53	$LiOH$	30 min.	20°	very slow	= 71.40:2(28.60)
	59	$BaCl_2$	30 min.	20°	very feeble	Ca:Ba = 57.89:42.11
	63	$SrCl_2$	30 min.	20°	very feeble	Ca:Sr = 28.57:71.42
	66	$MgSO_4$	30 min.	20°	moderate	0.006 per cent Ca
Magnesium	24	KOH	1 hour	35°	moderate	0.10 per cent K
	41	$NaOH$	1 hour	39°	slow	0.02 per cent Na
	55	$Li(Cl,OH)$	1 hour	31°	rapid	0.003 per cent Li
	61	$BaCl_2$	1 hour	24°	moderate	0.08 per cent Ba
	65	$SrCl_2$	1 hour	23°	rapid	0.0016 per cent Sr
	67	$CaCl_2$	1 hour	25°	rapid	Pure mercury

DISCUSSION OF RESULTS.

The electromotive series, in so far as concerns the metals under discussion, reads:

+K, Na, Li, Ba, Sr, Ca, Mg—.

Disregarding the action of water, we should expect each metal in this series, beginning at the positive end, to be capable of displacing from aqueous salt solutions any of the metals which follow it in the series, and, under like conditions, this displacement should take place the more readily, the farther apart the 2 metals stand in the series. In other words, applying our introductory considerations, and disregarding for the time being the action of water, we should expect, under like conditions, to have the relation,

$$\sqrt[+]{\frac{P_+}{p_+}} > \sqrt[n_-]{\frac{P_-}{p_-}},$$

and the more electropositive metal should displace the more electronegative one from its salt solutions. The relative magnitudes of the above 2 expressions, on which depends the direction of displacement, can be affected in 2 ways, with the possibility of reversing them entirely. First, the values of p_+ and p_- can be changed at will, by regulating the ionic concentrations and, second, the values of P_+ and P_- can be altered by substituting solutions of the metals in mercury for the metals themselves.

To take a concrete example, it appears very probable, from the results obtained, that finely divided barium could be made to precipitate potassium from a saturated solution of its hydroxide or carbonate, if it were not for the action of the displaced potassium, not to mention the barium, on the water of the solution. On providing for a lower solution pressure of the displaced potassium, however, by the substitution of barium amalgam for free barium, whereby the solution pressure of the barium is also lowered, the action of the water is greatly retarded, and the precipitation of potassium from certain of its salt solutions by barium may be accomplished readily.

In the case of barium amalgam and potassium chloride solution (Exp. 11), only a trace of potassium entered the amalgam. This was due, in part, to the fact that the barium which entered the solution remained dissolved, and also that the amalgamated metals, owing to the presence of hydrogen ions in the solution, were enabled to enter the solution by virtue of their action on the water. On reducing the ionic concentration of the barium to a minimum, by the substitution of a saturated solution of potassium sulphate in place of the chloride solution, many times the amount of potassium entered the amalgam (Exp. 12); but the actual quantity was in this case also very small. When, however, a high concentration of potassium ions was provided for and, at the same time, the ionic concentration of both barium and hydrogen were kept at a minimum, it was found that potassium readily entered the amalgam. These conditions were realized by the employment of a concentrated solution of potassium hydroxide, or carbonate (Exps. 13-14). The solubility product of the barium hydroxide, or carbonate formed was immediately exceeded in the corresponding solution and, owing to the hydroxyl ions present, the ionic concentration of hydrogen was so low in each case that no perceptible evolution of gas took place.

In this connection, it is interesting to compare the action of barium and strontium amalgams on saturated solutions of potassium and sodium chlorides and sulphates. While barium amalgam displaces the metals from these solutions only with great difficulty, they are readily displaced from the solutions by strontium amalgam. In other words, the values of the solution pressures of the alkali earth metals in these amalgams are of an inverse order as compared with those of the metals themselves. The same behavior is repeated by strontium and calcium in the action of their amalgams on lithium salt solutions.

Besides having confirmed certain consequences of Nernst's theory of electrolytic solution pressures, the results of this investigation have led to the solution of another important question, *viz.*, the nature of solutions of the metals of the alkali and alkali earth groups in mercury.

Assuming that these metals exist in dilute solution in the form of monatomic molecules, let us consider the case of equimolecular solutions of them in mercury. Under this assumption, we should expect the solution pressures of the dissolved metals to be similarly affected; they should all be correspondingly lowered, and the electromotive series should still read,

+K, Na, Li, Ba, Sr, Ca, Mg—.

However, it is apparent from the results obtained that such is no longer the case. In so far as can be judged from these results, the series reads,

+Mg, Li, Ca, K, Na, Sr, Ba—.

This irregular alteration of the solution pressures of the dissolved metals can only be accounted for by the assumption that, with the possible exception of magnesium, compounds of the metals and mercury exist, even in very dilute solution.

It may be added, however, that the solution pressures exerted by the alkali and alkali earth metals in these amalgams are possibly due to a partial dissociation of the compounds in solution. In the case of a relatively stable amalgam, like that of barium, this dissociation is evidently very slight, while in that of an unstable amalgam, *e. g.*, calcium amalgam, it is relatively greater.

SUMMARY.

It has been experimentally shown in the present investigation:

1. That the following 16 pairs of metals are reversibly displaceable in aqueous solutions: K–Na, K–Li, K–Ba, K–Sr, K–Ca, K–Mg; Na–Li, Na–Ba, Na–Sr, Na–Ca, Na–Mg; Li–Sr, Li–Ca; Ba–Mg; Sr-Ca, Sr–Mg.

2. That in the presence of mercury, lithium can be displaced from a mixed solution of its chloride and hydroxide by magnesium, with the formation of lithium amalgam. In like manner, barium can be displaced from its chloride solution by the amalgams of the more electronegative metals, strontium and calcium.

3. That, contrary to the generally accepted view, the metals

of the alkali and alkali earth groups, with the possible exception of magnesium, do not exist as such, in solution in mercury, in the form of monatomic molecules. The liquid amalgams of these metals are solutions in mercury of compounds of the general formula MHg_m, containing only 1 atom of the amalgamated metal to the molecule.

4. That the stability of these compounds increases in the following order: $LiHg_m$, KHg_m, $NaHg_m$, for the alkali compounds; and $CaHg_m$, $SrHg_m$, $BaHg_m$, for those of the alkali earths.

5. That the same equilibrium is obtained by the action of an equimolecular solution of sodium and potassium chlorides on either potassium, sodium, or lithium amalgam.

URBANA, ILLINOIS,
December 20, 1906.

OBITUARY.

MARCELLIN PIERRE EUGÈNE BERTHELOT.

Professor Berthelot was born in Paris, October 25, 1827, and died in the same city, from heart failure, a few hours after the death of his wife, March 18, 1907. Like Moissan, the whole of Berthelot's active life was spent in Paris. He received the Doctor degree from the University in 1854, was "Préparateur" in the Collège de France, 1859–76. In 1860 he became professor of organic chemistry at the École de Pharmacie and in 1865 a chair of theoretical chemistry was created for him in the Collège de France.

It is impossible to give, in a brief space, any adequate account of Berthelot's investigations; his original papers are numbered by the hundreds and include contributions to every branch of chemical science. In organic chemistry he is, perhaps, best known for his investigations into the nature of fats, for his synthetic work and his contributions to our knowledge of the terpenes. Although, of course, he did not discover acetylene, yet everything of importance that we know of its properties is due to his investigations. Analytical chemistry has also benefited by his labors. In the domain of explosives he was second to none, and it is due essentially to his work that France became equipped with smokeless powder. To Berthelot we owe an enormous quantity of thermo-chemical data and it is because of his supreme influence that French Inorganic Chemistry is essentially "thermic" and not "ionic."[1] His physical-chemical work extended much further, however, and included numerous investigations in electro-chemistry, the action of light, etc. Berthelot contributed largely to extending our knowledge of the chemistry of plants and animals, including the chemical activity of bacteria. In short, it may be said with truth that his contributions to any one branch of chemistry were each sufficient to earn for him no small measure of fame—how much more is due, therefore, for his contributions to all regions of the science?

Berthelot's activities were by no means confined to the laboratory, he was the author of numerous text-books and of many essays, reports, pamphlets, etc. Special mention must be made of his volumes on ancient alloys. His political activities are shown by his being Minister of Education, 1886–87, and Minister of Foreign Affairs, 1895-96. It is hardly necessary to add that he was a member of practically every government commission which had any connection with science. That his native country appreciated him is shown by his becoming a life Senator in 1882. He has been Secretary of the French Academy since 1889. In 1876 he was appointed Inspector-General of Higher Education.

Berthelot was a Foreign Associate of the National Academy of Sciences, a member of the American Philosophical Society, Honorary Member of the German and American Chemical Societies and a Foreign Member of the Chemical Society (London). He was elected a Foreign Member of the Royal Society in 1877 and subsequently received from it the Copley and Davy medals. In 1901 Berthelot received an international "medal of honor," in recognition of his position among French chemists and of his services to the science.

REPORT.

The Alkylation of Metallic Cyanides.

In a recent paper Guillemard[2] describes the results obtained when metallic cyanides are treated with alkyl oxides and methyl sulphates under varying conditions of temperature and for different periods of time. The amounts of cyanide and isocyanide formed are a function of the temperature and time, because the isocyanide, which is produced at low temperatures, is changed over to the more stable cyanide by continued heating at a higher temperature. The cyanides of potassium,

[1] Cf. THIS JOURNAL, 35, 470.
[2] Compt. rend , 144, 326.

silver, zinc, nickel, copper and mercury, the ferrocyanides of potassuim, lead and silver, and the ferricyanides of potassium and silver were used in the experiments. With potassium cyanide and ethyl iodide only the cyanide could be isolated, because the isocyanide which was first formed combined with the ethyl iodide. When the silver cyanide was used and the mixture was kept at 80°, for 4 hours, only isocyanide was obtained. If, however, the action was carried on at a higher temperature, for a longer time, a mixture of cyanide and isocyanide was produced, the quantity of isocyanide decreasing with rise in temperature. Nickel cyanide yielded only isocyanide below 140°, but above this temperature a mixture of cyanide and isocyanide. The conclusion, from a number of experiments, was that at low temperatures only the isocyanide was formed, at higher temperatures a mixture, and about certain temperatures only the cyanide. The author accepts the view advanced by Nef, that at ordinary temperatures all metallic cyanides should be represented by the formula MNC. He regards the formation of cyanides at high temperatures as due to a rearrangement of the isocyanide to form the more stable cyanide, this change being accompanied by evolution of heat. He gives, as an example of such a change, the formation of benzonitrile from diphenylthiourea or from formanilide. J. E. G.

REVIEWS.

A HISTORY OF CHEMICAL THEORIES AND LAWS. By M. M. PATTISON MUIR, M.A., Fellow and Prœlector in Chemistry of Gonville and Caius College, Cambridge. New York: John Wiley & Sons; London: Chapman & Hall, Limited. 1907. 8vo. pp. xx + 555. Price, Cloth, $4.00 net.

In his preface the author says: "I have not attempted the uncalled-for task of writing a history of chemistry. To do that, at present, would be to produce a mighty volume, containing a series of text-books, a bewildering catalogue of facts, a sheaf of biographical essays, supplemented by prolegomena, appendices, and chronological tables.

"The object of this book is to set forth what seemed to me the main lines along which the science of chemistry has advanced to its present position. In making an attempt to do this in an orderly fashion, with some fulness of detail, and, I hope, some sense of proportion, I have passed over very many able memoirs; I have not mentioned the chemical histories of particular substances, except in so far as these have appeared to me to illustrate the development of some law, theory, or hypothesis of general importance. I describe only those investigations which, in my judgment, have given powerful impulses to the advance of chemical science along paths already trodden, or have opened new ways of progress.''

In his introduction he says: ''The subject proper of this book will be dealt with broadly as follows:

''I. The history of the attempts to answer the question, What is a homogeneous substance?

The recognition of homogeneous substances, and the description of chemical changes as interactions of these substances;
The marks of elements and of compounds;
The laws of chemical combination, the atomic hypothesis, the molecular and atomic theory;
The more searching examination of the compositions of homogeneous substances, allotropy;
Elements which do not react;
Chemical nomenclature and notation.

''II. The history of the attempts to answer the question, What happens when homogeneous substances interact?

The classification of homogeneous substances;
Acids, bases, salts;
Radicals, types, dualism, the unitary hypothesis;
Chemical equivalency;
Isomerism and constitutional formulae;
Application of the hypothesis of ionization to the classification of homogeneous substances;
The conditions and general laws of chemical change;
Chemical affinity;
Chemical equilibrium;
The elucidation of chemical reaction by measurements of physical properties.''

This book can be conscientiously recommended to all chemists. It will repay a careful study, whether the chemist be old or young, provided he is interested in the history of the development of his science. It has the great advantage of being readable. The author has shown much skill in selecting material for treatment. By throwing emphasis upon the essentials he avoids confusion by passing over those things which, however interesting from some points of view, are not essential to the development of chemistry.

In the first chapter he gives a sketch of the progress of chemical conceptions from early times to the discovery of oxygen. Of course, this is a sketch. His first sentence is interesting. It is this: ''Chemistry is a universal science; it was founded by many whose memories are forgotten. The foundations of chemistry are laid deep in the experiences, in the hopes, the visions of mankind."

This is evidently suggested by the narrower statement of Würtz, which provoked so much adverse criticism nearly 40 years ago: "La chimie est une science française; elle est constitué par Lavoisier d'immortelle mémoire."

The principal results of the experiments of Priestley, Scheele, Lavoisier, Boyle, Cavendish, are well summarized in this chapter, which ends in these words: "It is not often that the power of destroying and the power of reconstructing are united in so extraordinary a degree as they were united in Lavoisier, the greatest of all chemists."

In the next chapter the work of Lavoisier is more fully and very clearly treated. Dalton's writings are skilfully and most satisfactorily presented. In regard to the atomic theory the author says: "Notwithstanding its incompleteness, Dalton's atomic theory is an immense help to the solution of the two fundamental questions of chemistry; indeed it would not be an exaggeration to say that the most important advances made in chemistry since the publication of the "*New System*" have been made by following lines of research suggested by applications of the atomic theory."

In a later chapter, which has to deal with elementary substances, the author again returns to Lavoisier, referring to him in these words: "Before the close of the alchemical period we find several exact students of nature who had gained fairly clear conceptions of composition; the most notable of these was Boyle."

"The preparation had been long and varied; suddenly, it seems to us, as we look back, chemistry began, fashioned from the materials which the centuries had gathered, by a man of supreme genius. Lavoisier was dowered by nature with the power of thinking accurately, and, as we say, scientifically. He did not free himself from the trammels of the phlogisteans; he was free-born."

Although the author disclaims any intention of writing "a history, either of physical chemistry or of chemical physics," he has succeeeded in presenting those features of this subject which are of most interest to what may distinctively be called chemistry, and even one who has not attempted to follow all the advances of physical chemistry would be able to see the bearings of the advances in this field on the progress of chemistry. But in this notice it is impossible to go into further details. Only by studying the book can any one form an adequate conception of it. It is well worth the study, and should take its place in the library of every earnest chemist. I. R.

A TEXT-BOOK OF ELEMENTARY ANALYTICAL CHEMISTRY, QUALITATIVE AND VOLUMETRIC. By JOHN H. LONG, M.S., SC.D., Professor of Chemistry and Director of the Chemical Laboratories in the Northwestern University Medical School. Third edition, revised and enlarged. Philadelphia: P. Blakiston's Son & Co. 1906. Price, $1.25 net.

The author states in the preface that, in this edition, several important additions have been made. Besides minor changes throughout the book, there has been added a chapter discussing reactions in solutions, in which such matters as chemical equilibrium, solubility product, hydrolysis, oxidation and reduction are included.

After treating the matter of qualitative analysis in the way found in most text-books on this subject, the author discusses the reactions of a few organic substances and the methods to be followed in the examination of poisons. In the portion devoted to quantitative analysis typical examples of the different varieties of quantitative methods, both volumetric and gravimetric, and the methods used in the analysis of water and some other common substances are given.

This book could be used to advantage with students who are only required to study chemistry for 2 years and wish, during this time, to get some knowledge of quantitative work in addition to the qualitative methods which are almost always studied in the second year. For medical students, for whom no doubt the volume is intended, the course here given would be well suited, provided the introduction of the quantitative work did not prevent them from taking a course in organic chemistry. J. E. G.

MONOGRAPHIEN ÜBER ANGEWANDTE ELEKTROCHEMIE. XXIV Band. Die Elektrochemischen Deutschen Reichspatente. Auszüge aus den Patentschriften gesammelt, geordnet und mit Hinweisen versehen von DR. P. FERCHLAND und DR. P. REHLÄNDER. Mit 124 Figuren im Text. Halle a. S.: Wilhelm Knapp. 1906. pp. 230. Price, M. 10.

This monograph is the result of much labor and skill expended in classifying, excerpting and criticizing the German patents. The list is complete to May, 1906.

The first section—inorganic—includes all patents for electrolytic production of the light metals, alkalis, halogens, bleaching liquids, oxidized salts (permanganates, percarbonates, etc.), barium and strontium hydroxides, carbides, ozone, nitrogen compounds, and the heavy metals and their derivatives. The section on organic work includes patents for making aniline, benzidine, paraminophenol, dyestuffs and pharmaceutical products. This is a valuable book of reference for chemists. E. R.

OUTLINES OF QUALITATIVE CHEMICAL ANALYSIS. By FRANK AUSTIN GOOCH, Professor of Chemistry in Yale University, and PHILIP EMBURY BROWNING, Assistant Professor of Chemistry in Yale University. First edition. New York: John Wiley & Sons. pp. 145. Price, $1.25 net.

This book is very elementary. The tabular method used in most manuals to show the separations of the ions in a given group is here also used to show the behavior of the ions toward reagents. The equations for all reactions used in separations are printed in full. The methods are, in the main, the common ones. E. R.

CONTRIBUTION A L'ÉTUDE DE LA SAPONIFICATION DES CORPS GRAS. Par M. MAURICE NICLOUX, Docteur ès Sciences, Docteur en Médecine, chef de Laboratoire a la Faculté de Médecine, Lauréat de l'Institut. etc. Paris: Librairie Scientifique, A. Hermann. 1906. pp. 76. Price, 3 Fr.

This monograph is devoted to an account of the author's researches on the fat hydrolyzing substance in the seeds of the castor oil plant. It is divided into 7 sections dealing, at some length, with the extraction of the active material and its lipolytic and hydrolytic powers under various conditions. The most important conclusion which is drawn is that the lipolytic activity is not due to a soluble diastatic ferment, but is inherent in the cytoplasm itself. This result is not in harmony with the conclusions of other workers in the same field.

J. B. T.

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SOLUBILITY. I.

BY E. C. BINGHAM.

The present paper presents the results of some experimental work performed in the Cavendish Laboratory, the work being preliminary to a more extended study of solubility.

All gases are completely miscible; liquids, therefore, afford an interesting field for study inasmuch as the liquid and gaseous states have been found to be continuous, but, of the enormous amount of work already done on solubility, the greater part has been confined to the study of a solid in a liquid, especially water. There are sufficient reasons, moreover, for believing that the solution of a solid may be more complex than the solution of a liquid, and that water may not show the phenomena of solution as simply as do some other liquids.

Alexejeff[1] was the first to make a systematic study of the solubility of liquids in liquids. He studied carefully the effect of variation of temperature upon the solubility of a few pairs of immiscible liquids. He found that, in general, the solubility increased with the temperature until, in a few cases, the solubility became infinite, *i. e.*, the liquids became completely miscible. This temperature was called by Masson[1] "the critical solution temperature," in analogy to the ordinary critical solution temperature. Later, Guthrie[2] found that in certain instances the solubility increased with falling temperature until there was complete miscibility. Such a temperature has been called, therefore, a "lower critical solution temperature."

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[1] Wied. Ann., **28**, 305 (1886).

Since Alexejeff's work, several others[3] have studied carefully certain pairs of liquids, but it does not seem to have occurred to any one as being worth while to make a systematic examination of a considerable number of representative liquids, to learn, if possible, under what conditions an immiscible combination may be looked for, and also when a change of temperature will cause the immiscible pairs to become miscible.

To test the above point and to accumulate data for further work, it seemed advisable to the author to make all the possible combinations with a certain number of pure liquids.

METHOD OF WORK.

Thick-walled glass tubing of about 2 mm. internal diameter was carefully cleaned by the use of chromic acid mixture, washed and dried. Several hundred small tubes, 6–7 mm. long, were then made, care being taken not to introduce moisture during the sealing off. The tubes were kept over phosphorus pentoxide until ready for use.

The substances employed were, as far as practicable, the best that Kahlbaum provides. In order to work readily with small quantities, I constructed a burette of small bore, graduating and calibrating it carefully. The tip was drawn out to a long, narrow tube, suitable for introducing the liquids to the bottom of the small tubes as well as for filling the burette without having the preparations come into contact with the air. The top of the burette was continually connected with a calcium chloride drying-tube, by means of a rubber tube of considerable length. The tubes were stoppered immediately after adding 1 of the components and the result of putting the 2 components together was noted as soon as possible, even during the process of bringing them together. Equal volumes of the 2 components were added together throughout. It was necessary to work with phenol in a pipette on account of its tendency to solidify. Resorcinol, benzoic acid, silver nitrate, sodium, phosphorus and sulphur were all added in the solid state. When necessary, the tubes were sealed before the blowpipe and then heated in a water or paraffin bath until mixture ensued, if possible. In some cases chemical reaction began at high temperatures, and in one case resulted in a severe explosion. The tubes were also cooled in an ice and salt mixture. Some 200 were cooled in liquid air.

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[1] Nature, Feb. 12, 1891; Z. physik. Chem., **7**, 500 (1891).

[2] Phil. Mag. [5], **18**, 29, 499 (1884).

[3] Rothmund: Z. physik. Chem., **26**, 433 (1898). Hudson: *Ibid.*, **47**, 113 (1904).

In the table the results of the experiments are given in concise form. The substances are arranged in the order of their molecular volumes. Those pairs which mixed completely are marked M, those which were immiscible at all the temperatures which were employed are marked I, in some cases with the temperature to which they were heated added. Upper critical solution temperatures are marked CT and lower critical solution temperatures with LCT, with the, roughly approximate, temperature at which the substances become miscible. ChR denotes that a chemical reaction took place between the components when brought together. In case this combination was very slow, conclusions in regard to miscibility could be obtained which are of interest. These cases are marked $\frac{\text{M}}{\text{ChR}}$; or $\frac{\text{ChR}}{\text{M}}$ in case the combination took place so rapidly that the results were in doubt. The results in italics were taken mainly from the papers of Rothmund,[1] Zawidski,[2] and the author,[3] also Watts' "Dictionary" and

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[1] Z. physik. Chem., **26**, 433 (1898).

[2] *Ibid.*, **35**, 202.

[3] This Journal, **34**, 481 (1905); **35**, 195 (1906).

		50 Olive oil	49 Castor oil	48 Paraffin	47 Oleic acid	46 Dekane	45 Isobutylisobutyrate	44 Triethylamine	43 Hexane	42 Acetophenone	41 Stannic chloride	40 m Toluidine	39 Toluene	38 Isoamyl alcohol	37 Nitrobenzene	36 Ether	35 Benzoic acid	34 Phenyl chloride	33 Benzoic aldehyde	32 Carbon tetrachloride	31 Valeric acid
Mercury	1	I	I	I	I	I	I	I	I	I	I	I	I	I	I	I	I	I	I	I	I
Phosphorus	2	I	I	I		I 250°	I	ChR	I 210°	I		I	I	I	I	I	I	CT 190°	I	I	I
Sulphur	3	I	I	I	I	I 260°	I	ChR I	I	I			CT 179°	I 226°	I	I	I	CT 117°	I	I 216°	I
Water	4	I	I	I	I	I	I	LCT 18.6	I	CT 220	M	I	I	I	I	I	CT 115	CT 220°	I	I 220°	I
Sodium	5			I		I 150°			I 170°							I				I	
Bromine	6	ChR	ChR		ChR	ChR M	ChR M	ChR	ChR M	ChR I	I	ChR	M	M	M	M?	M	M	M	M	M
Ammonia	7								I	M?	M		I	M	M?	M	M?			M	M?
Formic acid	8			I	I	I 220°	M	ChR	I 190°	M	M	M	I	M	M	M	M	CT 110°	M	CT 220°	M
Silver nitrate	9	I				I 230°		ChR	I		ChR	ChR	I		I	I	I	I 130°	ChR		I
Methyl alcohol	10			I		CT 76°	M	M	CT 428	M	M	M	M	M	M	M	M	M	M	M	M
Sulphur dioxide	11	CT 28°			CT 24°	CT 32°	M		CT 14°					M		M					M
Carbon dioxide	12													M	LCT -53	M					
Sulphuric acid	13					I	M	ChR	I	ChR	M	ChR	I	M	M	M	M	M	ChR	M	M
Acetic aldehyde	14		M	M	M	M	M	M	M	M	M	M ChR	M	M	M	M	M	M	M	M	M
Acetic acid	15		M	CT 200°	M	CT	M	ChR	CT -15°	M	M	M	M	M	M	M	M	M	M	M	M
Ethyl alcohol	16	CT 145	M	CT 103°	M	CT -15°	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M
Carbon disulphide	17	M	M	M		M	M	M	M	M	M ChR?	M	M	M	M	M	M	M	M	M	M
Methyl formate	18				M	CT	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M
Propionic nitrile	19				M	CT 40°	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M
Acetone	20	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M
Propionic acid	21				M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M
Glycerol	22				I	I	I 230°	I	I	I	M	I	I	CT 68°	I	I	M	I 260°	CT 100°	I 270°	M
Pyridine	23			M		M	M	M	M	M	M ChR	M	M	M	M	M	M	M	M	M	M
Chloroform	24	M	M	M	M	M	M	M	M	M	I 220°	M	M	M	M	M	M	M	M	M	M
Methylene iodide	25			CT 128°	CT 90°	CT 90°	M	ChR	CT	M	I	M	M	M	M	M	M	M	M	M	CT 73°
Benzene	26	M	M	M	M	M	M	M	M	M	I	M	M	M	M	M	M	M	M	M	M
Phenol	27				M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M
Aniline	28	M	M	CT 110°	M	CT 32°	M	M	CT 65°	M	ChR M	M	M	M	M ChR	M	M	M	M ChR	M	M
Isobutyric acid	29	M	M	M	M	M	M	M ChR	M	M	M	M	M	M	M	M	M	M	M	M	M
Resorcinol	30	CT 245	M		M	I 250°	M	M	CT 250°	M	M	M	CT 134°	M	M	M	M	CT 227°	M	M	M
Valeric acid	31	M	M	M	M	CT -20°	M	M ChR	M	M	CT -10°	M	M	M	M	M	M	M	M	M	31
Carbon tetrachloride	32	M	M	M		M	M	M	M	M	I 250°	M	M	M	M	M	M	M	M	32	
Benzoic aldehyde	33	M	M	M	M	M	M	M	M	M	M	M ChR	M	M	M	M	M	M	33		
Phenyl chloride	34	M	M	M		M	M	M	M	M	CT -15°	M	M	M	M	M	M	34			
Benzoic acid	35	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	35				
Ether	36	M	M	M		M	M	M	M	M	M	M	M	M	M	36					
Nitrobenzene	37	M	M		M	CT 275°	M	M	CT -15°	M	M	M	M	M	37						
Isoamyl alcohol	38	M	M	M	M	M	M	M	M	M	M	M	M	38							
Toluene	39	M	M	M	M	M	M	M	M	M	I	M	39								
m. Toluidine	40	M	M		M	CT 32°	M	M	M	M	ChR	40									
Stannic chloride	41			I	I	I	CT 170°	M	I	M	41										
Acetophenone	42			M		CT 10°	M	M	M	42											
Hexane	43	M	CT 35°	M		M	M	M	43												
Triethylamine	44					M	M	44													
Isobutyl isobutyrate	45	M	M	M			45														
Dekane	46			M		46															
Oleic acid	47	M	M	M	47																
Paraffin	48	M	M	48																	
Castor oil	49	M	49																		
Olive oil	50	50																			

Resorcinol 30	Isobutyric acid 29	Aniline 28	Phenol 27	Benzene 26	Methylene iodide 25	Chloroform 24	Pyridine 23	Glycerol 22	Propionic acid 21	Acetone 20	Propionic nitrile 19	Methyl formate 18	Carbondisulphide 17	Ethyl alcohol 16	Acetic acid 15	Acetic aldehyde 14	Sulphuric acid 13	Carbon dioxide 12	Sulphur dioxide 11	Methyl alcohol 10	Silver nitrate 9	Formic acid 8	Ammonia 7	Bromine 6	Sodium 5	Water 4	Sulphur 3	Phosphorus 2	Mercury 1
I	I	I	I	I		I	I	I	I	I	I	I	I	I	I	I	I			I	ChR	I	I	ChR	M	I	ChR	I	1
	I	CT 260°		CT 170°	M	I	I			I	I		M	I	I	I	I	$\underline{I}$	I	I	ChR	I	$\underline{M}$	ChR M?	ChR	I	M?	2	
I	I	$\underline{\text{CT}}$ 139°	I	$\underline{\text{CT}}$ 163°	$\underline{M}$	I	CT 150°	I		I	I		$\underline{M}$	I	I	I	I			I	ChR	I	$\underline{M}$	ChR M?	$\underline{\text{ChR}}$	I	3		
M	$\underline{\text{CT}}$ 248°	$\underline{\text{CT}}$ 167°	CT 688	$\underline{I}$	I	I	M	$\underline{M}$	$\underline{M}$	$\underline{M}$	CT 114	CT? ChR	$\underline{I}$	$\underline{M}$	$\underline{M}$	$\underline{M}$	$\underline{M}$	$\underline{M}$	$\underline{I}$	$\underline{M}$	M	$\underline{M}$	M	$\underline{I}$	$\underline{\text{ChR}}$	4			
	$\underline{\text{ChR}}$								$\underline{\text{ChR}}$					$\underline{\text{ChR}}$	$\underline{\text{ChR}}$	ChR	$\underline{\text{ChR}}$		ChR	$\underline{\text{ChR}}$	$\underline{\text{ChR}}$	$\underline{\text{ChR}}$	M?	$\underline{\text{ChR}}$	5				
ChR	M	ChR	ChR		ChR	$\underline{M}$	ChR	I		M	M		M	M	M	ChR	I	I		M	ChR	I		6					
$\underline{M}$?	$\underline{M}$?	$\underline{M}$	$\underline{M}$?	$\underline{M}$?		$\underline{M}$	$\underline{M}$	$\underline{M}$	$\underline{M}$?				$\underline{\text{ChR}}$	$\underline{M}$	$\underline{M}$?	$\underline{M}$				$\underline{M}$		$\underline{M}$	7						
M	M	M ChR	M	$\underline{\text{CT}}$	I	M		$\underline{\text{ChR}}$ M	M·	$\underline{\text{ChR}}$ M	$\underline{\text{ChR}}$ M	M	$\underline{I}$	M	M	M	$\underline{\text{ChR}}$		M	$\underline{\text{ChR}}$ M	ChR	8							
ChR	I	ChR	ChR	I									I	ChR	ChR					ChR	9								
M	M	M	M	$\underline{M}$	I	$\underline{M}$	M	M	M	$\underline{M}$	M	M	CT 405	$\underline{M}$	M	M	ChR	$\underline{M}$	M	10									
				M									M				I	$\underline{\text{CT}}$	11										
			$\underline{\text{ChR}}$	$\underline{M}$		$\underline{M}$							$\underline{M}$	$\underline{M}$	$\underline{M}$?			12											
ChR	M	ChR	ChR	CT		I	ChR	M	M	ChR M		$\underline{\text{ChR}}$ M	I 160°	ChR M	M	ChR	13												
M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	14													
M	M	M	M	M	CT 45°	M	M	M	M	M	M	M	CT -10°	M	15														
M	M	$\underline{M}$	M	$\underline{M}$	CT 22°	$\underline{M}$	M	$\underline{M}$	M	$\underline{M}$	M	M	CT -14°	16															
I	M	M	M	$\underline{M}$	M	M	M	I	M	$\underline{M}$	M	M	17																
M	M.	M	M	M	M	M	M	I	M	M	M	18																	
M	M	M	M	M	M	M	M	CT 140	M	M	19																		
M	M	M	M	$\underline{M}$	M	$\underline{M}$	M	M	M	20																			
M	M	M ChR	M	M	CT 52°	M	M	M	21																				
M	M	M	M	M	M	$\underline{I}$	M	22																					
M	M	M	M	M	M	M	23																						
CT 135°	M	M	M	$\underline{M}$	M	24																							
CT 180°	CT 15°	M	M	M	25																								
CT 109°	M	M	M	26																									
M	M	M	27																										
M	M	28																											
M	29																												
30																													

M = Miscible
I = Immiscible (to temperature given)
CT = Critical Solution Temperature
LCT = Lower Critical Solution Temperature.
ChR = Chemical Reaction.
Observations underlined are by other workers

Table of Miscibilities
of
Pairs of Substances
in the
Liquid State.

Beilstein's "Handbuch." The results for ammonia were taken from the work of Franklin and Kraus,[1] and those for carbon dioxide from the work of Büchner.[2]

DISCUSSION OF RESULTS.

The substances in the table, as stated above, have been arranged in the order of their molecular volumes, at the ordinary temperature, 20°, or at the melting point of the higher melting substance in case one or both of the substances are solid at the ordinary temperature. For various reasons it seemed to the author that this grouping might bring out some useful relations. Others have suggested association and dielectric constant as a basis of comparison. As a matter of fact the results do not differ so very widely whichever of these is made the basis of comparison, *i. e.*, the substances having large dielectric constants and high association are also, in general, substances of small molecular volume.

This arrangement causes most of the immiscible pairs to lie in the upper part, and especially the upper left of the table. In other words, substances of very small molecular volume, when mixed with other substances of larger molecular volume, are often immiscible with them. Water illustrates this fact admirably, for if it is brought into contact with various series of organic compounds, the solubility continually decreases as the molecular volume of the latter increases. With methyl alcohol, mol. vol. = 39.5, ethyl alcohol, mol. vol. = 57.9, and propyl alcohol, mol. vol. = 74.7, water is completely miscible. With secondary butyl alcohol, mol. vol. = 89.5, isobutyl alcohol, mol. vol. = 92.3, and isoamyl alcohol, mol. vol. = 105.5, water has a critical solution temperature. With the higher alcohols water is immiscible so far as I have been able to ascertain. Again, with formic acid, mol. vol. = 37.7, acetic acid, mol. vol. = 57.0 and propionic acid, mol. vol. = 74.3, water is completely miscible, but with butyric acid, mol. vol. = 91.7 and isobutyric acid, mol. vol. = 92.6, water has a critical solution temperature, while with valeric acid, mol. vol. = 93.6, and the higher acids it is immiscible so far as ascertained. Moreover, of the 2 isomeric butyric acids the one with the smaller molecular volume is miscible at the lower temperature.

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[1] THIS JOURNAL, **24**, 83 (1900).

[2] Z. physik. Chem., **54**, 665 (1906).

This comparison may be extended to other series—aldehydes, ketones and nitriles, but it is not necessary to pursue this line further at present.

Exceptions to the observation in the preceding paragraph occur, of course, in case the 2 components unite chemically. Thus bromine and sulphur can hardly be said to be miscible since there is evidently a union between them. So stannic chloride and water unite to form, not a mere physical mixture, but a chemical union, as evidenced by the great affinity between them and by the resulting hydrates which are formed.

It has been remarked that the immiscible pairs occur, for the most part, at the left of the table. If the first 10 substances are eliminated and thus the first 10 rows of the table, the remaining pairs are principally miscible at some temperature attained in the present series of experiments. The exceptions are noteworthy; they are nearly all pairs containing, as 1 component, sulphuric acid, glycerol, or stannic chloride. These substances, so markedly diverse in most properties, have yet one property in common, *i. e.*, a great affinity for water. Furthermore, the substances with which they are immiscible, as given in the table, are those materials which dissolve water very sparingly. With sulphuric acid the following substances are immiscible: sulphur dioxide, carbon disulphide, chloroform, toluene, hexane and dekane. Wiih stannic chloride are immiscible chloroform, methylene iotdde, benzene, carbon tetrachloride, toluene, hexane, dekane, oleic acid and paraffin. With glycerol are immiscible carbon disulphide, methyl formate, chloroform, phenyl chloride, ether, carbon tetrachloride, nitrobenzene, toluene, *m*-toluidine, acetophenone, hexane, triethylamine, isobutyl isobutyrate, dekane and oleic acid. It should be noted that no substance which is miscible with water is immiscible with sulphuric acid, stannic chloride, or glycerol. Moreover, many substances, in which water is only moderately soluble, are miscible with all

3 of these in the state of dehydration in which I obtained and used them.

The explanation of these exceptions would seem, then, to be incomplete dehydration. Propionic nitrile offers an interesting case in support of this explanation. Propionic nitrile and water have a critical solution temperature. Propionic nitrile and glycerol are immiscible at ordinary temperatures, hence they should mix at a somewhat elevated temperature if the above explanation is correct. As a matter of fact, they were found to become miscible at 140°.

An effort was made to dehydrate the glycerol by means of anhydrous copper sulphate in sealed tubes, heated and agitated for many weeks. This effort showed the presence of moisture by the hydration of the copper sulphate but the dehydration was evidently incomplete.

It may be asked why these substances, manifestly containing some water, were included in this table? The answer is, merely to be absolutely impartial in the choice of representative liquids as to all properties, of molecular weight, specific gravity, melting point, composition, association, dielectric constant, and it may now be shown that these results are not without interest in the light of other facts, because certain solubility data in the literature are quite contradictory as given in different places. These discrepancies may be partly explained by the above experiments. For example, it has been recorded that carbon disulphide is immiscible with ethyl alcohol. Rothmund showed that they are miscible, if pure, down to —14°. A slight amount of water present in the alcohol prevents miscibility.

Rothmund recorded that benzene and hexane form an immiscible pair. I have found them miscible to the lowest temperatures obtained with a freezing mixture. The data for benzene and chloroform seem contradictory as recorded by Watts and by Beilstein. I have noted that acetone and isobutyl isobutyrate are miscible down to —15° at least, but even on standing for a short time in an open tube, they become immiscible.

The above considerations lead me, therefore, to suggest the possible use of substances in which water is very sparingly soluble, such as ligroin, melted paraffin, or carbon disulphide to test the dehydration of organic liquids and easily fusible solids. If such substances are completely dehydrated, I believe that all except the first members of the series will be completely miscible. Thus in the table, formic acid and methyl alcohol are immiscible with paraffin. Acetic acid and paraffin are miscible at a somewhat elevated temperature. All the others are miscible at the ordinary temperature. It must be remembered that even after being dried as completely as possible, these contained a trace of water.

There are only 2 remaining exceptions to the entire miscibility of the approximately 700 pairs of substances obtained by combinations of the last 40 substances of the table. These exceptions are carbon disulphide and resorcinol and dekane and resorcinol. Further study will be devoted to these cases and to those pairs which gave critical solution temperatures.

CONCLUSIONS.

1. The miscibility or immiscibility of a large number of pairs of liquids has been tested.

2. It is found that substances of small molecular volume are often immiscible with other substances of large molecular volume.

3. It is pointed out that the presence of small amounts of water may often account for the immiscibility of substances. The possibility of utilizing this fact in obtaining a test for dehydration is suggested.

The author takes especial pleasure in thanking Prof. J. J. Thomson for advice and kindly criticism during the progress of this work and for the free use of the facilities of the Cavendish Laboratory.

CAMBRIDGE, ENGLAND,
July, 1906.

THE OSMOTIC PRESSURE OF GLUCOSE SOLUTIONS IN THE VICINITY OF THE FREEZING POINT OF WATER.[1]

By H. N. Morse, J. C. W. Frazer and F. M. Rogers.

The arrangements by means of which the low temperatures required for the present work were secured and maintained have been described in an earlier communication,[2] in which an account was given of the pressures exerted by cane sugar solutions in the neighborhood of 0°.

The material employed for the measurements, like that used in the first series of determinations with glucose,[3] was "Traubenzucker Kahlbaum." It was, however, distinctly less pure than that which was obtained on the former occasion. After aerating the pulverized substance and allowing it to stand in an exhausted desiccator until it gave no reaction for alcohol, it was found to have a somewhat uncertain melting point of 143°. Four determinations of carbon and hydrogen gave: for the former 40.28, 40.26, 40.35, and 40.35 instead of 39.98 per cent; and for the latter, 6.60, 6.66, 6.62, and 6.69 instead of 6.71 per cent. A solution[4] containing, in 100 cc. at 17°.5, 32.65 grams of the glucose gave a rotation of 101.45 instead of 100, saccharimeter degrees. The excessive rotation of the solutions and the abnormally high percentage of carbon led us to suspect the presence of dextrin, but no reaction for that substance could be obtained with iodine.

The material was then four times recrystallized by precipitating it with alcohol from its aqueous solutions. Thus purified, its melting point was found to be 145°–146°, instead of 146°, and the standard solution gave a rotation of 100.5 instead of 100 saccharimeter degrees. Two analyses gave: For the carbon, 40.09 and 39.96 instead of 39.98 per cent; and for the hydrogen, 6.64 and 6.77 instead of 6.71 per cent.

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[1] The work upon osmotic pressure which is in progress in this laboratory is aided by grants from the Carnegie Institution. The papers upon the subject which have preceded the present one will be found in this Journal, **26**, 80; **28**, 1; **29**, 173; **32**, 93; **34**, 1; **36**, 1, 39; **37**, 324 and 425.

[2] This Journal, **37**, 425.

[3] *Ibid.*, **37**, 329.

[4] Landolt, "Optische Drehungsvermögen," 448.

The record of the measurements of pressure are given with the customary fulness of detail in the following tables (I.–XX.). The results are stated in two ways, according to the two views which may be held regarding the proper method of correcting the observed pressures for the loss in rotation which the solutions suffer while in the cells. It has been intimated in a former paper[1] that probably *not less* than one-half of the loss in rotation is due to dilution which occurs while the cell is being opened, that is, to dilution which is subsequent to the measurement of the pressure. If this is true, the observed pressures should not be corrected for more than one-half the loss in rotation. In our opinion, the values given in the tables under "*Results, if corrected for one-half the loss in rotation,*" are more nearly correct than those presented under "*Results, if corrected for the whole loss in rotation.*"

With the record of each measurement there are given: 1, the *molecular osmotic pressure, i. e.*, the pressure divided by the weight-normal concentration of the solution; 2, *the ratio of the osmotic to the calculated gas pressure for the same temperature,* the volume of the gas being that of the solvent in the pure state; and 3, the *ratio of the observed molecular depression of the freezing point*[2] (Δ) of each solution to 1.85, the calculated molecular depression of the freezing point of water.

In Tables XXI. to XXV. the more important values recorded in Tables I. to XX. are brought together for greater convenience of comparison.

It will be noted (Table XXI., column 4) that the resistance of the membranes employed in the present series of measurements was greater than that recorded for the same cells in earlier work. The difference is due to the lower temperature at the time of deposition. The maximum resistance which a membrane in a given cell will exhibit is largely a matter of temperature; the lower the temperature is, the higher will be the resistance of the membrane. Of late, it has been our prac-

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[1] THIS JOURNAL, 37, 463.

[2] *Ibid.*, 37, 360.

Table I.

Original wt. normal concentration of solution, 0.1.
Rotation of original solution, 5°.22.
Rotation at conclusion of experiment, 5°.20.
Loss in concentration, 0°.02 = 0.38 per cent.
Calibration units of air in manometer, 495.09.
Time of setting up cell, 4.00 P.M., March 13, 1907.

Experiment No. 1.
Manometer used, 20.
Capillary depression, 0.02.
Cell used, D.
Resistance of membrane, 546,000.
Initial pressure, 1.43 atmospheres.

	Temperature.		Volume of air in manometer.		Corrections.						
Time.	Solution.	Air in manometer.	Uncorrected.	Corrected.	Atmospheric pressure.	Liquids in manometer.	Dilution of cell contents.	Capillary depression.	Osmotic pressure corrected.	Theoretical gas pressure.	Difference between pressure found and calculated.
March 13											
5.00 P.M.	0°.18	3°.70	242.02	238.78							
7.30 "	0°.18	1°.16	184.64	183.85							
11.00 "	0°.15	1°.06	170.17	169.51	0.99	0.43	0.01	0.02	2.39	2.23	0.16
March 14											
9.00 A.M.	0°.26	0°.82	169.40	168.89	1.00	0.43	0.01	0.02	2.39	2.23	0.16
12.30 P.M.	0°.32	0°.99	169.43	168.82	0.99	0.43	0.01	0.02	2.40	2.23	0.17
3.30 "	0°.38	1°.13	169.41	168.71	0.99	0.43	0.01	0.02	2.40	2.23	0.17
	0°.28										

Displacement of the manometer = 0.04 mm.

Results, if corrected for whole loss in rotation:
Correction = 0.01 atmosphere.
Osmotic pressure = 2.40 atmospheres.
Molecular pressure = 23.95 atmospheres.
Ratio of osmotic to gas pressure = 1.074.

Results, if corrected for half the loss in rotation:
Correction = 0.005 atmosphere.
Osmotic pressure = 2.39 atmospheres.
Molecular pressure = 23.90 atmospheres.
Ratio of osmotic to gas pressure = 1.071.
Ratio of Δ to 1.85 = 1.038.

Table II.

Original wt. normal concentration of solution, 0.1.
Rotation of original solution, 5°.22.
Rotation at conclusion of experiment, 5°.22.
Loss in concentration, 0°.00.
Calibration units of air in manometer, 478.16.
Time of setting up cell, 3.30 P.M., March 14, 1907.

Experiment No. 2.
Manometer used, No. 21.
Capillary depression, 0.02.
Cell used, G.
Resistance of membrane, 550,000.
Initial pressure, 2.13 atmospheres.

Time.	Temperature.		Volume of air in manometer.		Corrections.				Osmotic pressure corrected.	Theoretical gas pressure.	Difference between pressure found and calculated.
	Solution.	Air in manometer.	Uncorrected.	Corrected.	Atmospheric pressure.	Liquids in manometer.	Dilution of cell contents.	Capillary depression.			
March 14											
5.00 P.M.	0°.22	4°.80	176.62								
7.45 "	0°.20	0°.87	163.50								
11.15 "	0°.18	0°.69	159.08	158.68	1.00	0.37	0.00	0.02	2.40	2.23	0.17
March 15											
10.00 A.M.	0°.24	0°.57	158.43	158.10	1.01	0.37	0.00	0.02	2.40	2.23	0.17
12.30 P.M.	0°.25	0°.63	158.44	158.07	1.01	0.37	0.00	0.02	2.40	2.23	0.17
4.15 "	0°.28	0°.77	158.47	158.02	1.01	0.37	0.00	0.02	2.41	2.23	0.17
	0°.24										

Displacement of manometer = 0.17 mm.

Results, if corrected for whole loss in rotation:
Correction = 0.00.
Osmotic pressure = 2.40 atmospheres.
Molecular pressure = 24.03 atmospheres.
Ratio of osmotic to gas pressure = 1.077.

Results, if corrected for half the loss in rotation:
Correction = 0.00.
Osmotic pressure = 2.40 atmospheres.
Molecular pressure = 24.03 atmospheres.
Ratio of osmotic to gas pressure = 1.077.
Ratio of Δ to 1.85 = 1.038.

Table III.

Original wt. normal concentration of solution, 0.2.
Rotation of original solution, 10°.4.
Rotation at conclusion of experiment, 10°.3.
Loss in concentration, 0°.1 = 0.96 per cent.
Calibration units of air in manometer, 396.89.
Time of setting up cell, 4.30 P.M., Feb. 15, 1907.

Experiment No. 1.
Manometer used, No. 6.
Capillary depression, 0.02.
Cell used, G.
Resistance of membrane, 543,000.
Initial pressure, 4.30 atmospheres.

Time.	Temperature.		Volume of air in manometer.		Corrections.				Osmotic pressure corrected.	Theoretical gas pressure.	Difference between pressure found and calculated.
	Solution.	Air in manometer.	Uncorrected.	Corrected.	Atmospheric pressure.	Liquids in manometer.	Dilution of cell contents.	Capillary depression.			
Feb. 15											
6.00 P.M.	0°.12	1°.40	85.08								
9.00 "	0°.10	0°.79	79.87	79.64	1.00	0.60	0.05	0.02	4.65	4.45	0.20
11.30 "	0°.12	0°.72	79.75	79.54	1.00	0.60	0.05	0.02	4.66	4.45	0.21
Feb. 16											
8.30 A.M.	0°.12	0°.64	79.71	79.52	1.00	0.60	0.05	0.02	4.66	4.45	0.21
11.30 "	0°.12	0°.79	79.75	79.52	1.00	0.60	0.05	0.02	4.66	4.45	0.21
	0°.12										

Displacement of manometer = 0.05 mm.

Results, if corrected for whole loss in rotation:
Correction = 0.05 atmosphere.
Osmotic pressure = 4.66 atmospheres.
Molecular pressure = 23.29 atmospheres.
Ratio of osmotic to gas pressure = 1.047.

Results, if corrected for half the loss in rotation:
Correction = 0.025 atmosphere.
Osmotic pressure = 4.64 atmospheres.
Molecular pressure = 23.16 atmospheres.
Ratio of osmotic to gas pressure = 1.041.
Ratio of Δ to 1.85 = 1.038.

Table IV.

Original wt. normal concentration of solution, 0.2
Rotation of original solution, 10°.50.
Rotation at conclusion of experiment, 10°.45.
Loss in concentration, 0°.05 = 0.48 per cent.
Calibration units of air in manometer, 495.09.
Time of setting up cell, 3.45 P.M., Feb. 19, 1907.

Experiment No. 2.
Manometer used, No. 20.
Capillary depression, 0.02.
Cell used, D.
Resistance of membrane, 502,500.
Initial pressure, 4.07 atmospheres.

Time.	Temperature.		Volume of air in manometer.		Corrections.				Osmotic pressure corrected.	Theoretical gas pressure.	Difference between pressure found and calculated.
	Solution.	Air in manometer.	Uncorrected.	Corrected.	Atmospheric pressure.	Liquids in manometer.	Dilution of cell contents.	Capillary depression.			
Feb. 19											
5.45 P.M.	0°.12	2°.60	110.03	108.99							
8.00 "	0°.12	0°.96	98.08	97.73							
11.00 "	0°.12	0°.87	97.44	97.13	0.99	0.52	0.03	0.02	4.68	4.45	0.23
Feb. 20											
10.00 A.M.	0°.14	0°.75	97.48	97.21	0.99	0.52	0.03	0.02	4.67	4.45	0.22
1.00 P.M.	0°.14	0°.75	97.43	97.16	0.99	0.52	0.03	0.02	4.68	4.45	0.23
4.15 "	0°.12	0°.79	97.45	97.17	0.99	0.52	0.03	0.02	4.68	4.45	0.23
	0°.13										

Displacement of manometer = 0.04 mm.

Results, if corrected for whole loss in rotation:
Correction = 0.03 atmosphere.
Osmotic pressure = 4.68 atmospheres.
Molecular pressure = 23.39 atmospheres.
Ratio of osmotic to gas pressure = 1.051.

Results, if corrected for half the loss in rotation:
Correction = 0.015 atmosphere.
Osmotic pressure = 4.66 atmospheres.
Molecular pressure = 23.31 atmospheres.
Ratio of osmotic to gas pressure = 1.048.
Ratio of Δ to 1.85 = 1.038.

Table V.

Original wt. normal concentration of solution, 0.3.
Rotation of original solution, 15°.65.
Rotation at conclusion of experiment, 15°.55.
Loss in concentration, 0°.10 = 0.64 per cent.
Calibration units of air in manometer, 478.16.
Time of setting up cell, 12.30 P.M., Feb. 16, 1907.

Experiment No. 1.
Manometer used, No. 21.
Capillary depression, 0.02.
Cell used, D.
Resistance of membrane, 505,000.
Initial pressure, 5.91 atmospheres.

	Temperature.		Volume of air in manometer.		Corrections.						
Time.	Solution.	Air in manometer.	Uncorrected.	Corrected.	Atmospheric pressure.	Liquids in manometer.	Dilution of cell contents.	Capillary depression.	Osmotic pressure corrected.	Theoretical gas pressure.	Difference between pressure found and calculated.
Feb. 16											
1.15 P.M.	0°.15	2°.80	75.31	74.54							
5.30 "	0°.16	0°.96	64.37	64.14	0.99	0.50	0.05	0.02	7.03	6.68	0.35
8.00 "	0°.17	0°.98	64.31	64.08	0.99	0.50	0.05	0.02	7.04	6.68	0.36
11.45 "	0°.18	0°.94	64.28	64.06	0.99	0.50	0.05	0.02	7.04	6.68	0.36
Feb. 17											
9.30 A.M.	0°.24	0°.98	64.29	64.06	0.99	0.50	0.05	0.02	7.04	6.68	0.36
	0°.19										

Displacement of manometer = 0.16 mm.

Results, if corrected for whole loss in rotation:
Correction = 0.05 atmosphere.
Osmotic pressure = 7.04 atmospheres.
Molecular pressure = 23.45 atmospheres.
Ratio of osmotic to gas pressure = 1.054.

Results, if corrected for half the loss in rotation:
Correction = 0.025 atmosphere.
Osmotic pressure = 7.01 atmospheres.
Molecular pressure = 23.38 atmospheres.
Ratio of osmotic to gas pressure = 1.050.
Ratio of Δ to 1.85 = 1.038.

Table VI.

Original wt. normal concentration of solution, 0.3.
Rotation of original solution, 15°.53.
Rotation at conclusion of experiment, 15°.42.
Loss in concentration, 0°.11 = 0.71 per cent.
Calibration units of air in manometer, 478.16.
Time of setting up cell, 3.45 P.M., March 18, 1907.

Experiment No. 2.
Manometer used, No. 21.
Capillary depression, 0.02.
Cell used, G.
Resistance of membrane, 368,000.
Initial pressure, 5.83 atmospheres.

Time.	Temperature.		Volume of air in manometer.		Corrections.				Osmotic pressure corrected.	Theoretical gas pressure.	Difference between pressure found and calculated.
	Solution.	Air in manometer.	Uncorrected.	Corrected.	Atmospheric pressure.	Liquids in manometer.	Dilution of cell contents.	Capillary depression.			
March 18											
4.45 P.M.	0°.18	5°.00	76.96	75.57							
8.00 "	0°.17	0°.69	64.18	64.02	1.01	0.50	0.06	0.02	7.04	6.68	0.36
11.00 "	0°.18	0°.60	64.15	64.01	1.01	0.50	0.06	0.02	7.04	6.68	0.36
March 19											
10.15 A.M.	0°.23	0°.55	64.18	64.05	1.00	0.50	0.06	0.02	7.05	6.68	0.37
12.30 P.M.	0°.25	0°.55	64.20	64.07	1.00	0.50	0.06	0.02	7.04	6.69	0.35
3.00 "	0°.26	0°.60	64.20	64.06	0.99	0.50	0.06	0.02	7.05	6.69	0.36
	0°.25										

Displacement of manometer = 0.15 mm.

Results, if corrected for whole loss in rotation:
Correction = 0.06 atmosphere.
Osmotic pressure = 7.04 atmospheres.
Molecular pressure = 23.48 atmospheres.
Ratio of osmotic to gas pressure = 1.054.

Results, if corrected for half the loss in rotation:
Correction = 0.03 atmosphere.
Osmotic pressure = 7.01 atmospheres.
Molecular pressure = 23.38 atmospheres.
Ratio of osmotic to gas pressure = 1.049.
Ratio of Δ to 1.85 = 1.038.

Table VII.

Original wt. normal concentration of solution, 0.4.
Rotation of original solution, 20°.65.
Rotation at conclusion of experiment, 20°.50.
Loss in concentration, 0°.15 = 0.73 per cent.
Calibration units of air in manometer, 478.16.
Time of setting up cell, 4.30 P.M., Feb. 18, 1907.

Experiment No. 1.
Manometer used, No. 21.
Capillary depression, 0.02.
Cell used, G.
Resistance of membrane, 434,000.
Initial pressure, 9.09 atmospheres.

Time.	Temperature.		Volume of air in manometer.		Corrections.				Osmotic pressure corrected.	Theoretical gas pressure.	Difference between pressure found and calculated.
Feb. 18	Solution.	Air in manometer.	Uncorrected.	Corrected.	Atmospheric pressure.	Liquids in manometer.	Dilution of cell contents.	Capillary depression.			
6.00 P.M.	0°.14	2°.00	50.46	50.09							
8.00 "	0°.12	0°.91	49.26	49.09	1.00	0.52	0.08	0.02	9.36	8.91	0.45
11.15 "	0°.12	0°.76	49.23	49.09	1.00	0.52	0.08	0.02	9.36	8.91	0.45
Feb. 19											
10.15 A.M.	0°.12	0°.72	49.41	49.27	0.99	0.52	0.08	0.02	9.33	8.91	0.42
12.45 P.M.	0°.12	0°.80	49.38	49.23	0.98	0.52	0.08	0.02	9.35	8.91	0.44
4.00 "	0°.14	0°.93	49.44	49.27	0.98	0.52	0.08	0.02	9.34	8.91	0.43
	0°.13										

Displacement of manometer = 0.00.

Results, if corrected for whole loss in rotation:
Correction = 0.08 atmosphere.
Osmotic pressure = 9.35 atmospheres.
Molecular pressure = 23.37 atmospheres.
Ratio of osmotic to gas pressure = 1.049.

Results, if corrected for half the loss in rotation:
Correction = 0.04 atmosphere.
Osmotic pressure = 9.31 atmospheres.
Molecular pressure = 23.27 atmospheres.
Ratio of osmotic to gas pressure = 1.045.
Ratio of Δ to 1.85 = 1.038.

Table VIII.

Original wt. normal concentration of solution, 0.4.
Rotation of original solution, 20°.58.
Rotation at conclusion of experiment, 20°.40.
Loss in concentration, 0°.18 = 0°.87 per cent.
Calibration units of air in manometer, 495.09.
Time of setting up cell, 4.00 P.M., March 15, 1907.

Experiment No. 2.
Manometer used, No. 20.
Capillary depression, 0.02.
Cell used, D.
Resistance of membrane, 360,000.
Initial pressure, 7.25 atmospheres.

	Temperature.		Volume of air in manometer.		Corrections.						
Time.	Solution.	Air in manometer.	Uncorrected.	Corrected.	Atmospheric pressure.	Liquids in manometer.	Dilution of cell contents.	Capillary depression.	Osmotic pressure corrected.	Theoretical gas pressure.	Difference between pressure found and calculated.
March 15											
5.15 P.M.	0°.22	4°.60	65.69	64.59							
7.30 "	0°.20	0°.80	51.98	51.83							
11.00 "	0°.19	0°.69	51.46	51.33	1.01	0.58	0.09	0.02	9.33	8.91	0.42
March 16											
8.45 A.M.	0°.14	0°.54	51.39	51.29	1.01	0.58	0.09	0.02	9.33	8.91	0.42
5.00 P.M.	0°.30	0°.72	51.46	51.32	1.01	0.58	0.09	0.02	9.33	8.92	0.41
	0°.21										

Displacement of manometer = 0.34 mm.

Results, if corrected for whole loss in rotation:
Correction = 0.09 atmosphere.
Osmotic pressure = 9.33 atmospheres.
Molecular pressure = 23.33 atmospheres.
Ratio of osmotic to gas pressure = 1.047.

Results, if corrected for half the loss in rotation:
Correction = 0.045 atmosphere.
Osmotic pressure = 9.29 atmospheres.
Molecular pressure = 23.21 atmospheres.
Ratio of osmotic to gas pressure = 1.042.
Ratio of Δ to 1.85 = 1.038.

Table IX.

Original wt. normal concentration of solution, 0.5.
Rotation of original solution, 25°.55.
Rotation at conclusion of experiment, 25°.40.
Loss in concentration, 0.°15 = 0.58 per cent.
Calibration units of air in manometer, 495.09.
Time of setting up cell, 4.15 P.M., Mar. 11, 1907.

Experiment No. 1.
Manometer used, No 20.
Capillary depression, 0.02.
Cell used, D.
Resistance of membrane, 564,000.
Initial pressure, 10.00 atmospheres.

Time.	Temperature.		Volume of air in manometer.		Corrections.				Osmotic pressure corrected.	Theoretical gas pressure.	Difference between pressure found and calculated.
	Solution.	Air in manometer.	Uncorrected.	Corrected.	Atmospheric pressure.	Liquids in manometer.	Dilution of cell contents.	Capillary depression.			
March 11											
5.15 P.M.	0°.24	2°.30	48.10	47.70							
8.00 "	0°.17	0°.94	41.40	41.26	1.01	0.60	0.07	0.02	11.68	11.14	0.54
11.45 "	0°.12	0°.85	41.32	41.19	1.01	0.60	0.07	0.02	11.70	11.14	0.56
March 12											
10.00 A.M.	0°.17	0°.72	41.35	41.24	1.01	0.60	0.07	0.02	11.69	11.14	0.55
12.45 P.M.	0°.19	0°.86	41.35	41.21	1.00	0.60	0.07	0.02	11.70	11.14	0.56
3.30 "	0°.18	0°.94	41.36	41.22	1.00	0.60	0.07	0.02	11.70	11.14	0.56
	0°.17										

Displacement of manometer = 0.18 mm.

Results, if corrected for whole loss in rotation:
Correction =0.07 atmosphere.
Osmotic pressure = 11.69 atmospheres.
Molecular pressure = 23.39 atmospheres.
Ratio of osmotic to gas pressure = 1.050.

Results, if corrected for half the loss in rotation:
Correction = 0.035 atmosphere.
Osmotic pressure = 11.66 atmospheres.
Molecular pressure = 23.32 atmospheres.
Ratio of osmotic to gas pressure = 1.047.
Ratio of Δ to 1.85 = 1.038.

Table X.

Original wt. normal concentration of solution, 0.5.
Rotation of original solution, 25°.55.
Rotation at conclusion of experiment, 25°.30.
Loss in concentration, 0°.25 = 0.98 per cent.
Calibration units of air in manometer, 495.09.
Time of setting up cell, 4.00 P.M., Mar. 19, 1907.

Experiment No. 2.
Manometer used, No. 20.
Capillary depression, 0.02.
Cell used, D.
Resistance of membrane, 370,000.
Initial pressure, 9.82 atmospheres.

Time.	Temperature.		Volume of air in manometer.		Corrections.				Osmotic pressure corrected.	Theoretical gas pressure.	Difference between pressure found and calculated.
	Solution.	Air in manometer.	Uncorrected.	Corrected.	Atmospheric pressure.	Liquids in manometer.	Dilution of cell contents.	Capillary depression.			
March 19											
5.00 P.M.	0°.19	2°.60	48.97	48.51							
7.30 "	0°.14	0°.74	41.75	41.64							
11.00 "	0°.14	0°.71	41.57	41.46	0.98	0.60	0.12	0.02	11.70	11.14	0.56
March 20											
10.00 A.M.	0°.24	0°.57	41.59	41.50	0.99	0.60	0.12	0.02	11.68	11.14	0.54
1.00 P.M.	0°.27	0°.64	41.54	41.44	0.99	0.60	0.12	0.02	11.70	11.14	0.56
3.30 "	0°.29	0°.71	41.59	41.48	1.00	0.60	0.12	0.02	11.67	11.14	0.55
	0°.24										

Displacement of manometer = 0.06 mm.

Results, if corrected for whole loss in rotation:
Correction = 0.12 atmosphere.
Osmotic pressure = 11.69 atmospheres.
Molecular pressure = 23.38 atmospheres.
Ratio of osmotic to gas pressure = 1.049.

Results, if corrected for half the loss in rotation:
Correcton = 0.06 atmosphere.
Osmotic pressure = 11.63 atmospheres.
Molecular pressure = 23.26 atmospheres.
Ratio of osmotic to gas pressure = 1.044.
Ratio of Δ to 1.85 = 1.038.

Table XI.

Original wt. normal concentration of solution, 0.6.
Rotation of original solution, 30°.65.
Rotation at conclusion of experiment, 30°.10.
Loss in concentration, 0°.55 = 1.47 per cent.
Calibration units of air in manometer, 478.16.
Time of setting up cell, 4.00 P.M., Feb. 20, 1907.

Experiment No. 1.
Manometer used, No. 21.
Capillary depression, 0.02.
Cell used, B.
Resistance of membrane, 547,000.
Initial pressure, 12.93 atmospheres.

Time.	Temperature.		Volume of air in manometer.		Corrections.				Osmotic pressure corrected.	Theoretical gas pressure.	Difference between pressure found and calculated.
	Solution.	Air in manometer.	Uncorrected.	Corrected.	Atmospheric pressure.	Liquids in manometer.	Dilution of cell contents.	Capillary depression.			
Feb. 20											
5.30 P.M.	0°.12	1°.60	35.96	35.75							
7.30 "	0°.10	0°.86	33.58	33.47							
11.15 "	0°.08	0°.79	33.45	33.35	0.99	0.54	0.22	0.02	14.13	13.36	0.77
Feb. 21											
10.15 A.M.	0°.12	0°.72	33.52	33.43	0.99	0.54	0.22	0.02	14.09	13.36	0.73
1.00 P.M.	0°.14	0°.79	33.47	33.37	0.99	0.54	0.22	0.02	14.12	13.36	0.76
4.30 "	0°.14	0°.73	33.46	33.37	0.99	0.54	0.22	0.02	14.12	13.36	0.76
	0°.12										

Displacement of manometer = 0.06 mm.

Results, if corrected for whole loss in rotation:
Correction = 0.22 atmosphere.
Osmotic pressure = 14.12 atmospheres.
Molecular pressure = 23.53 atmospheres.
Ratio of osmotic to gas pressure = 1.057.

Results, if corrected for half the loss in rotation:
Correction = 0.11 atmosphere.
Osmotic pressure = 14.01 atmospheres.
Molecular pressure = 23.34 atmospheres.
Ratio of osmotic to gas pressure = 1.048.
Ratio of Δ to 1.85 = 1.038.

Table XII.

Original wt. normal concentration of solution, 0.6.
Rotation of original solution, 30°.55.
Rotation at conclusion of experiment, 30°.10
Loss in concentration, 0°.45 = 1.47 per cent.
Calibration units of air in manometer, 478.16.
Time of setting up cell, 4.15 P.M., Feb. 22, 1907.

Experiment No. 2.
Manometer used, No. 21.
Capillary depression, 0.02.
Cell used, G.
Resistance of membrane, 545,000.
Initial pressure, 13.64 atmospheres.

Time.	Temperature.		Volume of air in manometer.		Corrections.				Osmotic pressure corrected.	Theoretical gas pressure.	Difference between pressure found and calculated.
	Solution.	Air in manometer.	Uncorrected.	Corrected.	Atmospheric pressure.	Liquids in manometer.	Dilution of cell contents.	Capillary depression.			
Feb. 22											
5.30 P.M.	0°.06	1°.40	34.17	33.96							
8.00 "	0°.08	0°.49	33.37	33.31	1.02	0.54	0.22	0.02	14.11	13.36	0.78
11.30 "	0°.08	0°.43	33.30	33.25	1.02	0.54	0.22	0.02	14.14	13.36	0.75
Feb. 23											
10.30 A.M.	0°.08	0°.39	33.33	33.28	1.03	0.54	0.22	0.02	14.11	13.36	0.75
1.00 P.M.	0°.08	0°.46	33.36	33.30	1.02	0.54	0.22	0.02	14.11	13.36	0.75
4.30 "	0°.08	0°.50	33.36	33.30	1.02	0.54	0.22	0.02	14.11	13.36	0.75
	0°.08										

Displacement of manometer = 0.00.

Results, if corrected for whole loss in rotation:
Correction = 0.22 atmosphere.
Osmotic pressure = 14.12 atmospheres.
Molecular pressure = 23.53 atmospheres
Ratio of osmotic to gas pressure = 1.057.

Results, if corrected for half the loss in rotation:
Correction = 0.11 atmosphere.
Osmotic pressure = 14.01 atmospheres.
Molecular pressure = 23.34 atmospheres.
Ratio of osmotic to gas pressure = 1.048.
Ratio of Δ to 1.85 = 1.038.

Table XIII.

Original wt. normal concentration of solution, 0.7.
Rotation of original solution, 35°.30.
Rotation at conclusion of experiment, 34°.95.
Loss in concentration, 0°.35 = 0.99 per cent.
Calibration units of air in manometer, 495.09.
Time of setting up cell, 4.30 P.M., Feb. 21, 1907.

Experiment No. 1.
Manometer used, No. 20.
Capillary depression, 0.02.
Cell used, D.
Resistance of membrane, 364,000.
Initial pressure, 15.68 atmospheres.

Time.	Temperature.		Volume of air in manometer.		Corrections.				Osmotic pressure corrected.	Theoretical gas pressure.	Difference between pressure found and calculated.
	Solution.	Air in manometer.	Uncorrected.	Corrected.	Atmospheric pressure.	Liquids in manometer.	Dilution of cell contents.	Capillary depression.			
Feb. 21											
5.45 P.M.	0°.12	2°.00	31.07	30.84							
8.00 "	0°.10	0°.70	29.93	29.85							
Feb. 22											
12.45 A.M.	0°.10	0°.55	29.79	29.73	1.00	0.61	0.17	0.02	16.45	15.59	0.86
9.00 "	0°.06	0°.43	29.80	29.75	1.01	0.61	0.17	0.02	16.43	15.59	0.84
1.00 P.M.	0°.08	0°.43	29.79	29.74	1.01	0.61	0.17	0.02	16.44	15.59	0.85
4.00 "	0°.08	0°.49	29.77	29.72	1.01	0.61	0.17	0.02	16.45	15.59	0.86
	0°.08										

Displacement of manometer = 0.12 mm.

Results, if corrected for whole loss in rotation:
Correction = 0.17 atmosphere.
Osmotic pressure = 16.44 atmospheres.
Molecular pressure = 23.49 atmospheres.
Ratio of osmotic to gas pressure = 1.055.

Results, if corrected for half the loss in rotation:
Correction = 0.085 atmosphere.
Osmotic pressure = 16.36 atmospheres.
Molecular pressure = 23.37 atmospheres.
Ratio of osmotic to gas pressure = 1.049.
Ratio of Δ to 1.85 = 1.038.

Table XIV.

Original wt. normal concentration of solution, 0.7.
Rotation of original solution, 35°.25.
Rotation at conclusion of experiment, 35°.05.
Loss in concentration, 0°.20 = 0.57 per cent.
Calibration units of air in manometer, 495.09.
Time of setting up cell, 5.30 P.M., Feb. 23, 1907.

Experiment No. 2.
Manometer used, No. 20.
Capillary depression, 0.02.
Cell used, D.
Resistance of membrane, 365,000.
Initial pressure, 15.54 atmospheres.

	Temperature.		Volume of air in manometer.		Corrections.						
Time.	Solution.	Air in manometer.	Uncorrected.	Corrected.	Atmospheric pressure.	Liquids in manometer.	Dilution of cell contents.	Capillary depression.	Osmotic pressure corrected.	Theoretical gas pressure.	Difference between pressure found and calculated.
Feb. 23 6.30 P.M.	0°.06	0°.85	31.18	31.08							
8.15 "	0°.07	0°.59	29.75	29.69							
12.00 "	0°.06	0°.51	29.68	29.62	1.02	0.61	0.10	0.02	16.42	15.59	0.83
Feb. 24 10.15 A.M.	0°.06	0°.48	29.66	29.61	1.02	0.61	0.10	0.02	16.42	15.59	0.83
	0°.06										

Displacement of manometer = 0.00.

Results, if corrected for whole loss in rotation:
Correction = 0.10 atmosphere.
Osmotic pressure = 16.42 atmospheres.
Molecular pressure = 23.46 atmospheres.
Ratio of osmotic to gas pressure = 1.053.

Results, if corrected for half the loss in rotation:
Correction = 0.05 atmosphere.
Osmotic pressure = 16.37 atmospheres.
Molecular pressure = 23.39 atmospheres.
Ratio of osmotic to gas pressure = 1.050.
Ratio of Δ to 1.85 = 1.038.

Table XV.

Original wt. normal concentration of solution, 0.8.
Rotation of original solution, 39°.85.
Rotation at conclusion of experiment, 39°.40.
Loss in concentration, 0°.45 = 1.13 per cent.
Calibration units of air in manometer, 495.09.
Time of setting up cell, 3.45 P.M., Feb. 26, 1907.

Experiment No. 1.
Manometer used, No. 20.
Capillary depression, 0.02.
Cell used, G.
Resistance of membrane, 550,000.
Initial pressure, 17.52 atmospheres.

Time.	Temperature.		Volume of air in manometer.		Corrections.				Osmotic pressure corrected.	Theoretical gas pressure.	Difference between pressure found and calculated.
	Solution.	Air in manometer.	Uncorrected.	Corrected.	Atmospheric pressure.	Liquids in manometer.	Dilution of cell contents.	Capillary depression.			
Feb. 26											
5.00 P.M.	0°.12	2°.60	27.93	27.68							
8.00 "	0°.12	0°.73	26.18	26.11							
11.00 "	0°.12	0°.70	26.15	26.08	1.00	0.62	0.22	0.02	18.84	17.82	1.02
Feb. 27											
10.00 A.M.	0°.12	0°.75	26.15	26.08	1.00	0.62	0.22	0.02	18.84	17.82	1.02
1.00 P.M.	0°.15	0°.83	26.13	26.05	1.00	0.62	0.22	0.02	18.87	17.82	1.05
4.00 "	0°.14	0°.83	26.11	26.03	1.01	0.62	0.22	0.02	18.87	17.82	1.05
	0°.13										

Displacement of manometer = 0.20 mm.

Results, if corrected for whole loss in rotation:
Correction = 0.22 atmosphere.
Osmotic pressure = 18.86 atmospheres.
Molecular pressure = 23.57 atmospheres.
Ratio of osmotic to gas pressure = 1.058.

Results, if corrected for half the loss in rotation:
Correction = 0.11 atmosphere.
Osmotic pressure = 18.75 atmospheres.
Molecular pressure = 23.43 atmospheres.
Ratio of osmotic to gas pressure = 1.052.
Ratio of Δ to 1.85 = 1.038.

Table XVI.

Original wt. normal concentration of solution, 0.8.
Rotation of original solution, 39°.85.
Rotation at conclusion of experiment, 39°.50.
Loss in concentration, 0°.35 = 0.88 per cent.
Calibration units of air in manometer, 478.16.
Time of setting up cell, 4.00 P.M., Feb. 26, 1907.

Experiment No. 2.
Manometer used, No. 21.
Capillary depression, 0.02.
Cell used, D.
Resistance of membrane, 367,000.
Initial pressure, 17.36 atmospheres.

Time.	Temperature.		Volume of air in manometer.		Corrections.				Osmotic pressure corrected.	Theoretical gas pressure.	Difference between pressure found and calculated.
	Solution.	Air in manometer.	Uncorrected.	Corrected.	Atmospheric pressure.	Liquids in manometer.	Dilution of cell contents.	Capillary depression.			
Feb. 26											
5.00 P.M.	0°.12	2°.60	27.12	26.88							
8.00 "	0°.12	0°.73	25.10	25.03	1.00	0.55	0.17	0.02	18.84	17.82	1.02
11.00 "	0°.12	0°.70	25.02	24.96	1.00	0.55	0.17	0.02	18.90	17.82	1.08
Feb. 27											
10.00 A.M.	0°.12	0°.75	25.08	25.01	1.00	0.55	0.17	0.02	18.86	17.82	1.04
1.00 P.M.	0°.15	0°.83	25.10	25.02	1.00	0.55	0.17	0.02	18.85	17.82	1.03
4.00 "	0°.14	0°.83	25.09	25.01	1.01	0.55	0.17	0.02	18.85	17.82	1.03
	0°.13										

Displacement of manometer = 0.05. mm.

Results, if corrected for whole loss in rotation:
Correction = 0.17 atmosphere.
Osmotic pressure = 18.86 atmospheres.
Molecular pressure = 23.58 atmospheres.
Ratio of osmotic to gas pressure = 1.058.

Results, if corrected for half the loss in rotation:
Correction = 0.085 atmosphere.
Osmotic pressure = 17.78 atmospheres.
Molecular pressure = 23.47 atmospheres.
Ratio of osmotic to gas pressure = 1.054.
Ratio of Δ to 1.85 = 1.038.

Table XVII.

Original wt. normal concentration of solution, 0.9.
Rotation of original solution, 44°.40.
Rotation at conclusion of experiment, 43°.70.
Loss in concentration, 0°.70 = 1.58 per cent.
Calibration units of air in manometer, 495.09.
Time of setting up cell, 3.45 P.M., March 1, 1907.

Experiment No. 1.
Manometer used, No. 20.
Capillary depression, 0.02.
Cell used, G.
Resistance of membrane, 560,000.
Initial pressure, 19.55 atmospheres.

	Temperature.		Volume of air in manometer.		Corrections.						
Time.	Solution.	Air in manometer.	Uncorrected.	Corrected.	Atmospheric pressure.	Liquids in manometer.	Dilution of cell contents.	Capillary depression.	Osmotic pressure corrected.	Theoretical gas pressure.	Difference between pressure found and calculate d
March 1											
5.00 P.M.	0°.12	3°.50	25.19	24.87							
7.30 "	0°.12	0°.78	23.28	23.21							
11.00 "	0°.10	0°.73	23.24	23.18	1.00	0.62	0.35	0.02	21.35	20.05	1.30
March 2											
10.30 A.M.	0°.14	0°.86	23.25	23.18	0.99	0.62	0.35	0.02	21.36	20.05	1.31
12.45 P.M.	0°.16	1°.05	23.26	23.17	0.99	0.62	0.35	0.02	21.37	20.05	1.32
5.00 "	0°.24	1°.10	23.25	23.16	0.99	0.62	0.35	0.02	21.38	20.05	1.33
	0°.16										

Displacement of manometer = 0.15 mm.

Results, if corrected for whole loss in rotation:
Correction = 0.35 atmosphere.
Osmotic pressure = 21.37 atmospheres.
Molecular pressure = 23.74 atmospheres.
Ratio of osmotic to gas pressure = 1.066.

Results, if corrected for half the loss in rotation:
Correction = 0.175 atmosphere.
Osmotic pressure = 21.19 atmospheres.
Molecular pressure = 23.54 atmospheres.
Ratio of osmotic to gas pressure = 1.057.
Ratio of Δ to 1.85 = 1.038.

Table XVIII.

Original wt. normal concentration of solution, 0.9.
Rotation of original solution, 44°.40.
Rotation at conclusion of experiment, 44°.00.
Loss in concentration, 0°.40 = 0.91 per cent.
Calibration units of air in manometer, 478.16.
Time of setting up cell, 4.00 P.M. March 1, 1907.

Experiment No. 2.
Manometer used, No. 21.
Capillary depression, 0.02.
Cell used, D.
Resistance of membrane, 555,000.
Initial pressure, 20.77 atmospheres.

Time.	Temperature.		Volume of air in manometer.		Corrections.				Osmotic pressure corrected.	Theoretical gas pressure.	Difference between pressure found and calculated.
	Solution.	Air in manometer.	Uncorrected.	Corrected.	Atmospheric pressure.	Liquids in manometer.	Dilution of cell contents.	Capillary depression.			
March 1											
5.00 P.M.	0°.12	3°.50	23.98	23.68							
7.30 "	0°.12	0°.78	22.20	22.14	1.00	0.56	0.20	0.02	21.38	20.05	1.33
11.00 "	0°.10	0°.73	22.14	22.08	1.00	0.56	0.20	0.02	21.44	20.05	1.39
March 2											
10.45 A.M.	0°.14	0°.86	22.18	22.11	0.99	0.56	0.20	0.02	21.41	20.05	1.36
12.45 P.M.	0°.16	1°.05	22.24	22.15	0.99	0.56	0.20	0.02	21.38	20.05	1.33
5.00 "	0°.24	1°.10	22.24	22.15	0.99	0.56	0.20	0.02	21.38	20.05	1.33
	0°.15										

Displacement of manometer = 0.02 mm.

Results, if corrected for whole loss in rotation:
Correction = 0.20 atmosphere.
Osmotic pressure = 21.40 atmospheres.
Molecular pressure = 23.75 atmospheres.
Ratio of osmotic to gas pressure = 1.067.

Results, if corrected for half the loss in rotation:
Correction = 0.10 atmosphere.
Osmotic pressure = 21.30 atmospheres.
Molecular pressure = 23.66 atmospheres.
Ratio of osmotic to gas pressure = 1.062.
Ratio of Δ to 1.85 = 1.038.

Table XIX.

Original wt. normal concentration of solution, 1.0.
Rotation of original solution, 48°.90.
Rotation at conclusion of experiment, 48°.20.
Loss in concentration, 0°.70 = 1.43 per cent.
Calibration units of air in manometer, 495.09.
Time of setting up cell, 3.35 P.M., March 4, 1907.

Experiment No. 1.
Manometer used, No. 20.
Capillary depression, 0.02.
Cell used, D.
Resistance of membrane, 540,000.
Initial pressure, 22.33 atmospheres.

Time.	Temperature.		Volume of air in manometer.		Corrections.				Osmotic pressure corrected.	Theoretical gas pressure.	Difference between pressure found and calculated.
	Solution.	Air in manometer.	Uncorrected.	Corrected.	Atmospheric pressure.	Liquids in manometer.	Dilution of cell contents.	Capillary depression.			
March 4											
6.00 P.M.	0°.17	2°.40	22.01	21.82							
11.00 "	0°.12	0°.74	20.87	20.82	1.00	0.62	0.34	0.02	23.76	22.27	1.49
March 5											
8.50 A.M.	0°.16	0°.73	20.87	20.82	1.00	0.62	0.34	0.02	23.76	22.28	1.48
12.45 P.M.	0°.18	0°.90	20.88	20.81	1.00	0.62	0.34	0.02	23.77	22.28	1.49
4.15 "	0°.22	1°.07	20.90	20.82	0.99	0.62	0.34	0.02	23.77	22.28	1.49
	0°.17										

Displacement of manometer = 0.15 mm.

Results, if corrected for whole loss in rotation:
Correction = 0.34 atmosphere.
Osmotic pressure = 23.77 atmospheres.
Molecular pressure = 23.77 atmospheres.
Ratio of osmotic to gas pressure = 1.067.

Results, if corrected for half the loss in rotation:
Correction = 0.17 atmosphere.
Osmotic pressure = 23.60 atmospheres.
Molecular pressure = 23.60 atmospheres.
Ratio of osmotic to gas pressure = 1.059.
Ratio of Δ to 1.85 = 1.038.

Table XX.

Original wt. normal concentration of solution, 1.0.
Rotation of original solution, 48°.90.
Rotation at conclusion of experiment, 48°.32.
Loss in concentration, 0°.58 = 1.20 per cent.
Calibration units of air in manometer, 478.16.
Time of setting up cell, 4.15 P.M., March 4, 1907.

Experiment No. 2.
Manometer used, No. 21.
Capillary depression, 0.02.
Cell used, G.
Resistance of membrane, 540,000.
Initial pressure, 22.95 atmospheres.

	Temperature.		Volume of air in manometer.		Corrections.						
Time.	Solution.	Air in manometer.	Uncorrected.	Corrected.	Atmospheric pressure.	Liquids in manometer.	Dilution of cell contents.	Capillary depression-	Osmotic pressure corrected.	Theoretical gas pressure.	Difference between pressure found and calculated.
March 4 6.00 P.M.	0°.17	2°.40	20.64	20.46							
11.30 "	0°.12	0°.74	20.06	20.01	1.00	0.56	0.30	0.02	23.78	22.27	1.51
March 5 10.00 A.M.	0°.16	0°.85	20.11	20.05	1.00	0.56	0.30	0.02	23.73	22.28	1.45
12.45 P.M.	0°.18	0°.90	20.18	20.11	1.00	0.56	0.30	0.02	23.66	22.28	1.38
4.15 "	0°.22	1°.07	20.17	20.09	0.99	0.56	0.30	0.02	23.69	22.28	1.41
	0°.17										

Displacement of manometer = 0.09 mm.

Results, if corrected for whole loss in rotation:
Correction = 0.30 atmosphere.
Osmotic pressure = 23.72 atmospheres.
Molecular pressure = 23.72 atmospheres.
Ratio of osmotic to gas pressure = 1.064.

Results, if corrected for half the loss in rotation:
Correction = 0.15 atmosphere.
Osmotic pressure = 23.57 atmospheres.
Molecular pressure = 23.57 atmospheres.
Ratio of osmotic to gas pressure = 1.055.
Ratio of Δ to 1.85 = 1.038.

Table XXI.

Weight normal concentration.	No. of experiment.	Cell used.	Resistance of the membrane. Ohms.	Displacement of the manometer. mm.	Loss in rotation.		Pressure equivalent of loss in rotation. Atmosphere.
					Degree.	Per cent.	
1	2	3	4	5	6	7	8
0.1	1	D	546,000	0.04	0.02	0.38	0.01
"	2	G	550,000	0.17	0.00	0.00	0.00
0.2	1	G	543,000	0.05	0.10	0.96	0.05
"	2	D	502,500	0.04	0.05	0.48	0.03
0.3	1	D	505,000	0.16	0.10	0.64	0.05
"	2	G	368,000	0.15	0.11	0.71	0.06
0.4	1	G	434,000	0.00	0.15	0.73	0.08
"	2	D	360,000	0.34	0.18	0.87	0.09
0.5	1	D	564,000	0.18	0.15	0.58	0.07
"	2	D	370,000	0.06	0.25	0.98	0.12
0.6	1	B	547,000	0.06	0.55	1.47	0.22
"	2	G	545,000	0.00	0.45	1.47	0.22
0.7	1	D	364,000	0.12	0.35	0.99	0.17
"	2	D	365,000	0.00	0.20	0.57	0.10
0.8	1	G	550,000	0.20	0.45	1.13	0.22
"	2	D	367,000	0.05	0.35	0.88	0.17
0.9	1	G	560,000	0.15	0.70	1.58	0.35
"	2	D	555,000	0.02	0.40	0.91	0.20
1.0	1	D	540,000	0.15	0.70	1.43	0.34
"	2	G	540,000	0.09	0.58	1.20	0.30
						0.90	

tice to deposit the greater portion of the membrane at room temperature, and to complete the operation at whatever temperature the measurement of pressure was to be made. Care is also taken to keep the cell with the finished membrane at the same temperature until it is filled and closed. The solutions, at the time of filling, have always the temperature of the baths in which the cells are to be placed.

The slipping of the manometers in the rubber stoppers, with possible distortion of the latter, has been referred to[1] as a troublesome phenomenon in the earlier work, which, in the more recent measurements, had been largely overcome[2] by improvements in method and manipulation. Still further

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[1] THIS JOURNAL, **36**, 23, 50; **37**, 328 and 460.

[2] *Ibid.*, **37**, 460.

Table XXII.—Results for Each Experiment, if Correction Is Made for the Whole Loss in Rotation.

Weight normal concentration. 1	No. of experiment. 2	Temperature. 3	Correction. Atmospheres. 4	Osmotic pressure. Atmospheres. 5	Calculated gas pressure. Atmospheres. 6	Molecular osmotic pressure. Atmospheres. 7	Molecular gas pressure. Atmospheres. 8	Ratio of osmotic to gas pressure. 9
0.1	1	0°.28	0.01	2.40	2.23	23.95	22.28	1.074
“	2	0°.24	0.00	2.40	2.23	24.03	“	1.077
0.2	1	0°.12	0.05	4.66	4.45	23.29	“	1.047
“	2	0°.13	0.03	4.68	4.45	23.39	“	1.051
0.3	1	0°.19	0.05	7.04	6.68	23.45	“	1.054
“	2	0°.25	0.06	7.04	6.68	23.48	“	1.054
0.4	1	0°.13	0.08	9.35	8.91	23.37	“	1.049
“	2	0°.23	0.09	9.33	8.91	23.33	“	1.047
0.5	1	0°.17	0.07	11.69	11.14	23.39	“	1.050
“	2	0°.24	0.12	11.69	11.14	23.38	“	1.049
0.6	1	0°.12	0.22	14.12	13.36	23.53	“	1.057
“	2	0°.08	0.22	14.12	13.36	23.53	“	1.057
0.7	1	0°.08	0.17	16.44	15.59	23.49	“	1.055
“	2	0°.06	0.10	16.42	15.59	23.46	“	1.053
0.8	1	0°.13	0.22	18.86	17.82	23.57	“	1.058
“	2	0°.13	0.17	18.86	17.82	23.58	“	1.058
0.9	1	0°.16	0.35	21.37	20.05	23.74	“	1.066
“	2	0°.15	0.20	21.40	20.05	23.75	“	1.067
1.0	1	0°.17	0.34	23.77	22.28	23.77	“	1.067
“	2	0°.17	0.30	23.72	22.28	23.72	“	1.064

Mean ratio = 1.058

Table XXIII.—Results for Each Concentration, if Correction Is Made for the Whole Loss in Rotation

Weight normal concentration. 1	Temperature. 2	Osmotic pressure. Atmospheres. 3	Calculated gas pressure. Atmospheres. 4	Molecular osmotic pressure. Atmospheres. 5	Molecular gas pressure. Atmospheres. 6	Ratio of osmotic to gas pressure. 7
0.1	0°.26	2.40	2.23	23.99	22.28	1.076
0.2	0°.13	4.67	4.45	23.34	"	1.049
0.3	0°.22	7.04	6.68	23.47	"	1.054
0.4	0°.17	9.34	8.91	23.35	"	1.048
0.5	0°.21	11.69	11.14	23.39	"	1.050
0.6	0°.10	14.12	13.36	23.53	"	1.057
0.7	0°.07	16.43	15.59	23.48	"	1.054
0.8	0°.13	18.86	17.82	23.58	"	1.058
0.9	0°.16	21.39	20.05	23.75	"	1.067
1.0	0°.17	23.75	22.28	23.75	"	1.066

Mean ratio = 1.058

progress has been made in this direction, as will be seen on inspecting column 5 of Table XXI. In the present series the displacement of the manometers was less than ever before, and is wholly negligible as a source of dilution of the cell contents.

Dilution, due to the sucking in of water from the wall[1] while the cell is being closed at the beginning, and opened at the conclusion, of an experiment continues to affect our results, but in a considerably diminished degree, as will be seen by inspecting columns 6, 7 and 8 of Table XXI. The correction for dilution (column 8) is less than on any previous occasion; and, owing to the elimination of the dilution due to manometer displacements, it is of a much less uncertain character than formerly. The loss in the rotation of the solutions while in the cells, which is the measure of the dilution from all causes, has shown a gratifying decrease from the first. In the earliest series[2] of measurements in which the polariscope was used, it amounted to 2.8 per cent; in the second,[3] to 1.49 per cent; and in the third,[4] to 1.47 per cent. In the present series

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[1] THIS JOURNAL, **36**, 26, 49; **37**, 327.

[2] *Ibid.*, **36**, 39.

[3] *Ibid.*, **37**, 324.

[4] *Ibid.*, **37**, 425.

Table XXIV.—Results for Each Experiment, if Correction Is Made for Half the Loss in Rotation.

Weight normal concentration. 1	No. of experiment. 2	Temperature. 3	Correction. Atmospheres. 4	Osmotic pressure. Atmospheres. 5	Calculated gas pressure. Atmospheres. 6	Molecular osmotic pressure. Atmospheres. 7	Molecular gas pressure. Atmospheres. 8	Ratio of osmotic to gas pressure. 9	Ratio of Δ to 1.85. 10
0.1	1	0°.28	0.005	2.39	2.23	23.90	22.28	1.071	1.038
"	2	0°.24	0.000	2.40	2.23	24.03	"	1.077	"
0.2	1	0°.12	0.025	4.64	4.45	23.16	"	1.041	"
"	2	0°.13	0.015	4.66	4.45	23.31	"	1.048	"
0.3	1	0°.19	0.025	7.01	6.68	23.38	"	1.050	"
"	2	0°.25	0.030	7.01	6.68	23.38	"	1.049	"
0.4	1	0°.13	0.040	9.31	8.91	23.27	"	1.045	"
"	2	0°.21	0.045	9.29	8.91	23.21	"	1.042	"
0.5	1	0°.17	0.035	11.66	11.14	23.32	"	1.047	"
"	2	0°.24	0.060	11.63	11.14	23.26	"	1.044	"
0.6	1	0°.12	0.110	14.01	13.36	23.34	"	1.048	"
"	2	0°.08	0.110	14.01	13.36	23.34	"	1.048	"
0.7	1	0°.08	0.085	16.36	15.59	23.37	"	1.049	"
"	2	0°.06	0.050	16.37	15.59	23.39	"	1.050	"
0.8	1	0°.13	0.110	18.75	17.82	23.43	"	1.052	"
"	2	0°.13	0.085	18.78	17.82	23.47	"	1.054	"
0.9	1	0°.16	0.175	21.19	20.05	23.54	"	1.057	"
"	2	0°.15	0.100	21.30	20.05	23.66	"	1.062	"
1.0	1	0°.17	0.170	23.60	22.28	23.60	"	1.059	"
"	2	0°.17	0.150	23.57	22.28	23.57	"	1.055	"

Ratio of Δ to 1.84 = 1.044

Mean ratio = 1.052

Table XXV.—Results for Each Concentration, if Correction Is Made for Half the Loss in Rotation.

Weight normal concentration. 1	Temperature. 2	Osmotic pressure. Atmospheres. 3	Calculated gas pressure. Atmospheres. 4	Molecular osmotic pressure. Atmospheres. 5	Molecular gas pressure. Atmospheres. 6	Ratio of osmotic to gas pressure. 7	Ratio of Δ to 1.85. 8
0.1	0°.26	2.40	2.23	23.97	22.28	1.074	1.038
0.2	0°.13	4.65	4.45	23.24	"	1.045	"
0.3	0°.22	7.01	6.68	23.38	"	1.050	"
0.4	0°.17	9.30	8.91	23.24	"	1.044	"
0.5	0°.21	11.65	11.14	23.29	"	1.046	"
0.6	0°.10	14.01	13.36	23.34	"	1.048	"
0.7	0°.07	16.37	15.59	23.38	"	1.050	"
0.8	0°.13	18.77	17.82	23.45	"	1.053	"
0.9	0°.16	21.25	20.05	23.60	"	1.060	"
1.0	0°.17	23.59	22.28	23.59	"	1.057	"

Ratio of Δ to 1.84=1.044 Mean ratio = 1.052

the average loss amounts to only 0.90 per cent of the original rotation. The improvement is due to the elimination of manometer displacement already referred to, to increased rapidity of manipulation, and to the practice, recently introduced,[1] of dipping the cells before closing, and again before opening them, in a solution of sugar, the concentration of which is equivalent to that of the solution within the cell. The suppression of the dilution of the cell contents appears to us the most important of the problems of method which remain to be solved. It is hoped that this can be accomplished by so changing the construction of the cells that they can be more quickly opened or closed, and by diminishing the area of the membrane as compared with the capacity of the cell.

The results, as they would be if correction is made for the whole loss in rotation, are brought together in Tables XXII. and XXIII., and again in Tables XXIV. and XXV., as they would be if correction is made for only one-half the loss in rotation. The reason for believing the results as presented in Tables XXIV. and XXV. the more nearly correct ones has already been given,[1] but it will be restated. The dilution of the solutions which causes nearly all the loss in rotation occurs at two separate periods: First, while the cells are being closed; and second, while they are being opened. The former affects the observed osmotic pressure, and a correction for it is to be applied, if possible; while the latter is without effect upon the measurement and is to be neglected. The observed loss in rotation, however, covers all dilution and it is not practicable to ascertain precisely what proportion of it occurred during the first period, *i. e.*, while the cell was being closed. Formerly, the time required to open a cell was about equal to that consumed in closing it, and for this reason alone it was assumed to be safe to correct for only one-half the observed loss in rotation. That in so doing we did not undercorrect the results appeared probable from the fact that during the closing period the contents of a cell are constantly under considerably increased pressure, while during the opening period they are continuously under diminished pressure, which latter condition necessarily facilitates the entrance of water from the wet wall of the cell. We did not, however, rest with this solution of the problem. A careful record was kept of the time consumed in closing and opening each cell. On comparing these records with the observed losses in rotation, it was clear that more dilution occurs in a given time while a cell is being opened than while it is being closed. Of late we have been able to reduce the time required to open a cell as compared with that consumed in closing it, but not sufficiently, up to the present time, to justify us in correcting for more than one-half the loss of rotation.

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[1] This Journal, 37, 464.

It will be seen in Tables XXII., XXIII., XXIV. and XXV that, in the vicinity of 0°, the osmotic pressure of glucose solutions considerably exceeds the calculated gas pressure for the same temperatures. In this respect the conduct of glucose is analogous to that of cane sugar.[2] The divergence from gas pressure is, however, greater and also more irregular in the case of cane sugar than in that of glucose.

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[1] THIS JOURNAL, **37**, 463.

[2] *Ibid.*, **37**, 425.

The ratio of osmotic to gas pressure (Table XXII., column 9; XXIII., column 6; XXIV., column 9; XXV., column 7) appears to be largest in the case of the 0.1 weight-normal solution, to decrease somewhat and then to increase slightly with increasing concentration. A similar but more marked relation was observed in the case of cane sugar.[1] We do not, however, regard this relation as well established for glucose. The variations are not large, and they are such, we believe, as our experimental errors would be likely to produce. It has been stated in former papers that we add a small quantity of potassium ferrocyanide to the sugar solutions (8.46 mg. to 100 grams of water) and a supposed osmotically equivalent quantity (12.48 mg. to 100 grams of solvent) of copper sulphate to the water in which the cell is located during a measurement. Doubt has also been expressed[2] as to the exact osmotic equality of these concentrations of the membrane formers. Recent determinations of the freezing points of potassium ferrocyanide solutions[3] indicate a higher degree of dissociation than has hitherto been ascribed to that substance. Moreover, we have observed that when smaller quantities of the membrane formers are used in determining the osmotic pressure of dilute solutions, slightly lower pressures are obtained, which suggests that the ferrocyanide, in the quantity usually employed, exerts a somewhat greater osmotic pressure than the copper sulphate. Any overpressure on the part of the ferrocyanide, though small absolutely, would affect very decidedly, in the case of the 0.1 normal solution, such relative values as the molecular osmotic pressure, the ratio of osmotic to gas pressure, etc. The same is true of certain possible experimental errors of a constant character. The effect of such errors would diminish rapidly with increasing concentration—sinking to one-half in the case of the 0.2 normal, and becoming insignificant in that of the higher members of the series. We are therefore prepared, in the course of later work, to find for the 0.1 normal solution a smaller ratio of osmotic to gas pressure than that given in the tables, namely, 1.074. It would seem to be an easy matter to determine the osmotic inequality of the membrane formers, but we have found it otherwise. They cannot be omitted, and when we have tried to solve the problem by varying the quantities used, *e. g.*, by reducing them to one-half, the results have not been satisfactorily concordant. A possible explanation of the observed lack of agreement among the results of supposedly equivalent experiments is to be found in the fact that probably varying numbers of the ferrocyanogen ions are used up in repairing the membranes. It is to be remembered that the values in question amount, at most, to only a few—possibly 4 or 5—hundredths of an atmosphere.

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[1] This Journal, **37**, 425.

[2] *Ibid.*, **37**, 466.

[3] *Ibid.*, **34**, 311.

The effect of errors of calibration and of reading, on the other hand, increase with the concentration of the solutions, and, on that account, we are also prepared for some slight revision of the osmotic-gas ratios at the other end of the series. We should expect to find about the same degree of concordance among these ratios as is observed in solutions of equal concentration in respect to the molecular depression of the freezing point.[1]

The question which first suggests itself concerns the relation of the excess of osmotic over gas pressure to the difference between the values 1.92 and 1.85, the former number representing the observed molecular depression of the freezing point of weight-normal solutions of glucose, and the latter, the calculated molecular depression of the freezing point of water. For the purpose of such a comparison, column 10 has been added to Table XXIV, and column 8 to Table XXV, under the head of "*Ratio of* Δ *to* 1.85." There is also given the "*Ratio of* Δ *to* 1.84" (the Raoult or experimental value for the molecular depression of the freezing point of water). The value of Δ was found to vary between 1.92 and 1.91 within weight-normal concentrations ranging from 0.1 to 1.0, but it has been assumed to be constant at 1.92.

The ratio of Δ to 1.85 is 1.038, and that of Δ to 1.84 is 1.044; while the mean ratio of observed osmotic to calculated gas pressure is 1.052. Except in the case of the 0.1 normal solution, the variation of the individual ratios from the mean value 1.052 is not large, and we have given our reasons for thinking that later work will establish a somewhat smaller ratio for that concentration.

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[1] THIS JOURNAL, 37, 360.

The various ratios which have been presented are sufficiently in accord to justify the suspicion that, in the case of glucose solutions, the excess of osmotic over gas pressures in the vicinity of 0°, and the difference between the observed and the calculated depressions of the freezing points are to be referred to one and the same cause. Perfect agreement between these ratios could not be expected because of differences of temperature. The osmotic pressures were determined at temperatures ranging from +0°.06 to +0°.28, while the freezing points lie between —0°.192 and —1°.92.

We shall also compare the excessive osmotic pressures which cane sugar solutions were found to exert in the vicinity of 0° with their so-called abnormal freezing points; but, before entering upon that subject, it is necessary to explain a change in our views regarding the amount of *inversion* which takes place in the cell.

In the first series of measurements of the osmotic pressure of cane sugar solutions,[1] it was attempted to determine the inversion which occurred in the closed cells by the method of Fehling.[2] The quantities of invert sugar which were found in this way were small, insufficient, in fact, to justify any corrections for the concentrations 0.1 to 0.5. From 0.5 to 1.0, on the other hand, the results were more definite, and corrections ranging in value from 0.02 to 0.05 atmosphere were applied to the higher concentrations. We stated[3] at the time that we were "inclined to believe that the inversion of the cane sugar in the more concentrated solutions was greater than it was apparently found to be by the method which was employed to determine it," and that when the work was repeated "the polariscope, instead of Fehling's solution" would be "used to measure the inversion which has taken place in the cell."

On remeasuring the osmotic pressure of cane sugar solutions a year later,[1] with systematic use of the polariscope, it was found that the loss in rotation was in all experiments greater than could have been anticipated from the quantities of invert sugar which had been found in the previous work by the method of Fehling. It was assumed[2] (overhastily, as appeared later) that the greater portion of the loss in rotation was to be ascribed to *inversion*, and accordingly the results (so far as loss in rotation was concerned) were corrected for inversion only, except in those instances in which a definite amount of *dilution* could be ascribed to manometer displacements. If called upon to deal with the same data at the present time, we should give an alternative statement of results, in which one-half the loss in rotation—after deducting that accounted for by manometer displacement—was ascribed to dilution. The results as stated in the original paper are doubtless somewhat too low, because, in most instances, the whole loss in rotation is ascribed to inversion, and no correction is made for dilution. On the other hand, the results as presented in the alternative statement mentioned above would be too high because of the neglect to correct for inversion. The true osmotic pressures of the solutions will, we think, be found to lie somewhere between the two limits, *i. e.*, between the values obtained by ascribing the whole loss in rotation to *inversion* and those obtained by attributing one-half of it to *dilution*. It will be recalled here that the average extent of the debatable ground in the case in question amounts to 2.8 per cent of the observed pressures. The results, as stated in the original paper, are probably too low by about 1.5 per cent.

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[1] THIS JOURNAL, **34**, 1.

[2] *Ibid.*, **34**, 31.

[3] *Ibid.*, **34**, 92.

The fact that the solutions were probably diluted by water entering from the porous walls while the cells were being closed and opened did not escape attention,[3] but the amount of dilution from this cause was underestimated in the earlier work.

When the measurement of the pressure of glucose[4] solutions was taken up, it was found that the average loss in rotation was 1.49 per cent, notwithstanding considerable improvements which had been made in manipulation. It was this observation which convinced us that we had hitherto ascribed too much of the loss in the rotation of cane sugar solutions to *inversion* and too little to the *dilution* resulting from the sucking in of water from the wall while closing and opening the cell. In the case of glucose, *inversion* was excluded, and all loss of rotation must be ascribed to *dilution* resulting from manometer displacements, or from water acquired from the cell wall during the closing and opening periods.

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[1] THIS JOURNAL, **36**, 39.

[2] *Ibid.*, **36**, 41, 48.

[3] *Ibid.*, **36**, 26, 49.

[4] *Ibid.*, **37**, 324.

In Series III. of the measurements of the pressures of cane sugar, which are to be used in the comparison which follows, there was no considerable displacement of the manometers, and the average loss in rotation amounted to 1.47 per cent, as against 0.90 per cent for the corresponding glucose series. The difference is not wholly due to inversion of the cane sugar, but is partly accounted for by the fact that only about half of the cells were "dipped" in the former case, while in the latter all of them were subjected to that treatment. Under the circumstances, it is probable that no error is made in assuming that the greater portion of the loss in rotation, which was observed while measuring the pressures of cane sugar solutions in the vicinity of 0°, was due to dilution rather than to inversion. The observation that, when due allowance is made for improved manipulation as the work progresses, the loss of rotation in cane sugar solutions does not greatly exceed that of glucose solutions caused us, in the paper[1] upon the osmotic pressure of cane sugar solutions in the vicinity of 0°, to state the results in three ways, namely, as they would be: (1) If all loss in rotation is ascribed to inversion; (2) if all loss in rotation is ascribed to dilution; and (3) if one-half the loss in rotation is corrected as dilution. We also stated our conviction that the true pressures would be found to lie between the values found by the first and the third methods. At the present time we can add that the results obtained by correcting one-half the loss in rotation as dilution and neglecting inversion are, in our opinion, very nearly accurate.

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[1] THIS JOURNAL, 37, 425.

Table XXVI.—Results for Each Concentration, if Correction Is Made for Half the Loss in Rotation. Cane Sugar. Series III.

Weight normal concentration. 1	Temperature. 2	Osmotic pressure. Atmospheres. 3	Calculated gas pressure. Atmospheres. 4	Molecular osmotic pressure. Atmospheres. 5	Molecular gas pressure. Atmospheres. 6	Molecular depression of the freezing point. 7	Ratio of Δ to 1.84. 8	Ratio of Δ to 1.85. 9	Ratio of osmotic to gas pressure. 10
0.1	0°.24	2.44	2.23	24.40	22.29	1°.95	1.060	1.054	1.094
0.2	0°.26	4.80	4.46	24.00	“	1°.96	1.065	1.059	1.076
0.3	0°.22	7.16	6.69	23.87	“	1°.95	1.060	1.054	1.071
0.4	0°.24	9.40	8.92	23.50	“	1°.96	1.065	1.059	1.054
0.5	0°.19	11.85	11.14	23.70	“	1°.97	1.071	1.065	1.064
0.6	0°.22	14.25	13.37	23.75	“	1°.98	1.076	1.070	1.066
0.7	0°.23	16.81	15.60	24.01	“	1°.99	1.081	1.076	1.078
0.8	0°.23	19.33	17.83	24.16	“	2°.02	1.098	1.092	1.084
0.9	0°.27	22.13	20.06	24.59	“	2°.03	1.103	1.097	1.103
1.0	0°.25	24.78	22.28	24.78	“	2°.07	1.125	1.119	1.112

Having explained the change of view which has been forced upon us regarding the relative importance of inversion and dilution as causes of loss in rotation, we present Table XXVI. to show how the osmotic pressures in the vicinity of 0° and the freezing points of cane sugar solutions are related to one another with respect to the excess of the former over gas pressure, and the deviation of the latter from the calculated value of 1.85 or the experimental value 1.84.

It will be seen that in the case of the 0.1, 0.2 and 0.3 weight-normal concentrations the ratio of osmotic to gas pressure (column 10) differs considerably from that of Δ to 1.85 (column 9), but that the two ratios are in quite close agreement throughout the remainder of the series. We have already given our reasons[1] for thinking that the osmotic-gas ratios for the most dilute solutions will hereafter be diminished, which would bring them more nearly into agreement with the ratios of Δ to 1.85 or 1.84.

Attention is also called to Table XXVII., which brings out clearly the mutual relations of glucose and cane sugar with respect to the osmotic pressures and freezing points of their equivalent solutions.

If we represent by

P, the osmotic pressure of glucose,

P_1, the osmotic pressure of cane sugar,

Δ, the observed molecular depression of the freezing point of glucose,

Δ_1, the observed molecular depression of the freezing point of cane sugar,

R, the ratio of osmotic to gas pressure for glucose,

R_1, the ratio of osmotic to gas pressure for cane sugar,

then proportions, such as the following, should be found to hold approximately:

1. $P:P_1::\Delta:\Delta_1$;
2. $R:R_1::\Delta:\Delta_1$;
3. $R:R_1::\frac{\Delta}{1.85}:\frac{\Delta_1}{1.85}$; etc.

How they do hold for the proportion $P:P_1::\Delta:\Delta_1$ (and consequently for all other proper methods of comparison) is shown in Table XXVII. Exact agreement between the calculated and experimental values is not to be expected, owing to differences of temperature, and the divergences between them should increase with the concentration.

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[1] THIS JOURNAL, 37, 466.

Table XXVII.

Weight normal concentration.	P, osmotic pressure of glucose.	P_1, osmotic pressure of cane sugar.	Δ observed molecular depression of the freezing point of glucose.	Δ_1 molecular depression of the freezing point of cane sugar.	
				Calculated.	Observed.
0.1	2.40	2.44	1.92	1.95	1.95
0.2	4.65	4.80	“	1.98	1.96
0.3	7.01	7.16	“	1.96	1.95
0.4	9.30	9.40	“	1.94	1.96
0.5	11.65	11.85	“	1.95	1.97
0.6	14.01	14.25	“	1.95	1.98
0.7	16.37	16.81	“	1.97	1.99
0.8	18.77	19.33	“	1.98	2.02
0.9	21.25	22.13	“	2.00	2.03
1.0	23.59	24.78	“	2.02	2.07

It appears to have been established by the results published in this paper and the preceding one[1] that, in the vicinity of the freezing point of the solvent, both glucose and cane sugar solutions exert osmotic pressures which differ from the calculated gas pressures in about the same degree that the observed depressions of the freezing points of such solutions differ from those which are calculated by means of the value 1.85.

In view of this conclusion, it is now important to measure, in the vicinity of 0°, the osmotic pressures of the solutions of some substance of which the observed molecular depression of the freezing point is approximately 1.85. It is to be anticipated that such solutions, in the vicinity of the freezing point of water, will be found to exhibit osmotic pressures more in accord with the calculated gas pressures than are those of glucose and cane sugar. We shall undertake this as soon as we have succeeded in suppressing dilution in the cell. Until that has been accomplished, our work is necessarily limited to substances, the concentration of whose solutions can be readily and accurately determined after their removal from the cell.

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[1] This Journal, 37, 425

While engaged in the development of a method for the measurement of osmotic pressure, we were frequently assured that there was "*no need*" of such a method, that osmotic pressure could be determined by the freezing point method "*much more readily and far more accurately*" than by any method of direct measurement which could possibly be devised. Moreover, it is made apparent, from time to time, in the current literature, that this idea respecting the sufficiency of the freezing point method as a means of determining osmotic pressure continues to prevail in certain quarters. It may, therefore, not be amiss to recall here one of several of the erroneous conclusions regarding the osmotic pressures of glucose and cane sugar solutions to which the established freezing point data have led. One chemist, who apparently was fully convinced of the adequacy of the freezing point method of determining osmotic pressure, predicted that the pressure of a *volume-normal* solution of cane sugar would be found to be "*just about 35 atmospheres.*" The course of reasoning by which the conclusion was reached may be explained as follows: The theoretical value of Δ is 1.85, but the observed value is 2.66. The estimated gas pressure of a gram-molecular weight of cane sugar at —2°.66 (with a volume of 1 liter) is about 22.08 atmospheres. The osmotic pressure at —2°.66 will therefore be $\frac{2.66}{1.85} \times 22.08$, or 31.75 atmospheres. At 24°, since osmotic and gas pressure have the same (?) temperature coefficient, the osmotic pressure of a volume-normal solution of cane sugar will be $31.75 + 31.75 \times 0.00366 \times 26.66$, or 34.85 atmospheres.

The conclusion is erroneous by more than 3 atmospheres. The *volume-normal* solution (equivalent to the 1.26806 *weight-normal* solution) of cane sugar exerts an osmotic pressure, at 24°, of just about 31.5 atmospheres. The great error in the above estimate lies in the assumption that, having predicted from freezing point data a certain osmotic pressure at the temperature of freezing, the pressure at higher temperatures can be calculated by the law of Gay-Lussac for gases. We are not to be understood as denying that the law of Gay-Lussac does hold for osmotic pressure. On the contrary, we are inclined to believe that, with certain restrictions, it does hold, and that the pressure anomalies which appear at low temperatures will be found to disappear gradually at higher temperatures, until osmotic and gas pressures are in accord with respect to temperature coefficient. This, however, is a matter of opinion which has no value, except as it is fortified by experimental proof. The only evidence which we can offer at present is the fact that, in the vicinity of 20°, the osmotic pressures of cane sugar and glucose solutions have been found to agree very closely with those calculated for gases, provided we accept the volume of the solvent, and not that of the solution, as the standard for the gases.

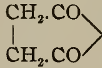
It may be affirmed, in concluding, that though the results presented in this paper and in the preceding one show that the osmotic pressures of glucose and cane sugar solutions in the vicinity of 0° could have been calculated from the freezing points with approximate correctness, any prediction, based upon the same data and the law of Gay-Lussac, as to their pressures at higher temperatures would have been wholly futile. This is true even when the calculations are based upon the weight-normal system for osmotic pressure. To illustrate: The osmotic pressure of the weight-normal solution of cane sugar at about 0° (exactly 0°.25) is 24.78 atmospheres. Its pressure at 24° would be estimated ($24.78 + 24.78 \times 0.00366 \times 23.75 = 26.93$) at 26.93 atmospheres. The observed pressure lies between 24.24 and 24.84 atmospheres, according to the method which is adopted for the correction of the loss in rotation in the cell.

JOHNS HOPKINS UNIVERSITY,
March 27, 1907.

PREPARATION OF THE ANILINE DERIVATIVES OF SUCCINIC ACID AND OF PHTHALIC ACID.

By J. Bishop Tingle and Marshall P. Cram.

In the course of some work on the nitration of certain aniline derivatives, which is being carried out by one of us in conjunction with Mr. F. C. Blanck in this laboratory,[1] it was necessary to prepare fairly large quantities of the aniline compounds of succinic and phthalic acids. Some of the methods which we have employed for this purpose differ in certain respects from those described in the literature; in two cases they are entirely new; moreover, they have all proved to be thoroughly satisfactory and adequate for our purpose, consequently it appears to be desirable to place them on record.

Succinanil,  $\begin{matrix}CH_2.CO\\ |\\ CH_2.CO\end{matrix}\!\!>\!NC_6H_5$, was prepared essentially according to the method of Menschutkin,[2] but the mixture of acid, 45 grams, and aniline, 40 grams, was placed in a small retort and heated for 3–4 hours, at 140°–150°, in a paraffin-bath. By this means the water was steadily eliminated and there was absolutely none of the "bumping" which was a source of trouble to Menschutkin. As soon as the action is completed, the retort is removed from the bath and quickly heated by a direct flame. A little aniline and water pass over and then the anil. If the distillation is conducted as rapidly as possible there is no danger of the retort's neck becoming closed. The yield is practically quantitative; from 270 grams of the acid we obtained 330 grams of anil, once recrystallized from alcohol.

The conversion of succinanil into SUCCINANILIC ACID,

$$C_6H_5NHCOCH_2CH_2COOH,$$

was carried out according to the directions of Menschutkin,[3] by heating the anil with milk of lime, in slight excess. Vigorous boiling for 10 or 15 minutes is necessary to bring the calcium salt into solution. The crystals which form on cooling are separated, treated with hydrochloric acid and the precipitated anilic acid is recrystallized once from water. The yield is 129 grams of purified material from 200 grams of anil.

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[1] This Journal, **36**, 605 (1906).

[2] Ann. Chem. (Liebig), **162**, 166 (1872).

[3] *Ibid.*, **162**, 178 (1872).

Laurent and Gerhardt discovered SUCCINANILIDE,

$$C_6H_5NHCOCH_2CH_2CONHC_6H_5,$$

as a by-product in the preparation of succinanil.[1] Menschutkin,[2] who repeated their work, found that, contrary to the statement of Laurent and Gerhardt, one recrystallization from alcohol was quite inadequate for the purification of the substance. He accomplished this by the use of alcoholic potassium hydroxide, which readily acts on the anil, but leaves the anilide unchanged. The yield is very poor. Laurent and Gerhardt only isolated a "small quantity," and Menschutkin obtained 22 grams of crude material from 40 grams of acid and 70 grams of aniline. We find that the anilide can be easily prepared by heating succinanilic acid, 50 grams, with aniline, 40 grams, in a reflux apparatus at 180°, during 5 working days. The product was treated twice with excess of cold, dilute hydrochloric acid to remove the unchanged aniline and, after being washed with water, was boiled for about 5 minutes with a clear filtered potassium hydroxide solution, consisting of 12 grams of stick potash in 250 cc. of 95 per cent alcohol, to dissolve any succinanil and succinanilic acid which might be present. Finally, it was recrystallized from alcohol. The yield was 17.1 grams of purified material, *i. e.*, 24.8 per cent of the theoretical quantity. We think that the yield might have been improved by heating the mixture of succinanilic acid and aniline under pressure, but a steel bomb was not available and the use of sealed tubes would have involved a good deal of extra trouble. Some little time after the completion of this part of our work, Arnold Reissert and Arnold More[1] described a method of preparing malonanilide by boiling ethyl malonate with aniline for a short time and then distilling off the alcohol as it is produced. They do not appear to have tested the behavior of ethyl succinate under these conditions. We are indebted to Mr. H. N. Morse for carrying out an experiment with ethyl succinate and aniline, according to the method of Reissert and More. After boiling these substances for about 30 minutes with a reflux condenser, the condenser was reversed and the material slowly distilled. The heat was applied by means of a bath containing sulphuric acid. The distillate consisted chiefly of aniline, in quantity almost equal to that originally used. The residue contained a relatively large amount of ethyl succinate, together with a small quantity of solid. The results of this experiment indicate, therefore, that the procedure of Reissert and More is not applicable to ethyl succinate and that our method for preparing succinanilide is superior to any which has, hitherto, been described.

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[1] Ann. chim. phys. [3], **24**, 179 (1848); Ann. Chem. (Liebig), **68**, 29 (1848).

[2] *Ibid.*, **162**, 187 (1872).

[3] Ber. d. chem. Ges., **39**, 3300 (1906).

Preparation of the Aniline Derivatives of Phthalic Acid.

Of the various methods which have been suggested for the preparation of PHTHALANIL, that of Zincke and Cooksey[1] appeared to us to be the most convenient. It consists in adding the necessary quantity of aniline to a glacial acetic acid solution of phthalic acid, and allowing the mixture to remain for some hours at the ordinary temperature. When we attempted to carry out this experiment we found that the solubility of phthalic acid in glacial acetic acid is so very small, being only about 1.7 grams in 100 grams, at the ordinary temperature, that the preparation of the quantity of material which we needed would have involved a, relatively, very large expenditure of time and acetic acid. Our experiments were, therefore, conducted as follows: Phthalic acid, 200 grams = 1 mol. and glacial acetic acid, 500 grams, were mixed and aniline, 112 grams = 1 mol., was added. After heating this material on a water-bath during 2 working days, water was added and the product filtered. The residue consisted of a mixture which could not be separated by repeated extraction with alcohol. In these circumstances, the portion which had not dissolved in alcohol and the part which deposited on cooling the alcoholic solution were mixed, and boiled for 10 minutes with a solution of 20 grams of dry sodium carbonate in 500 cc. of water. A portion dissolved; the remainder, after being washed and dried, weighed 100 grams and melted at 203°–206°; it was, therefore, practically pure phthalanil, for which Zincke and Cooksey[1] give the melting point 203° and Dobner[2] 205°. The former chemists omit all reference to the yield which they obtained, whereas the latter reports a "theoretical yield" by the distillation of phthalic anhydride and aniline. The yield by our method, as already noted, is 50 per cent of the phthalic acid employed, and if we were repeating our preparation we should omit the treatment with alcohol and boil the precipitate from the diluted acetic acid directly with sodium carbonate. Even with this simplification our method does not appear to be as good as Döbner's, though it is decidedly superior to that of Zincke and Cooksey. There is no indication in the paper of their reason for ignoring Döbner's method, but they state distinctly that "heating should be avoided." Having obtained all the material which we needed we did not consider it necessary to repeat Döbner's work. If there is ground for distrusting it, then our method appears to be the best and most convenient hitherto suggested for the preparation of phthalanil.

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[1] Ann. Chem. (Liebig), 255, 375 (1889).

At a later stage of our investigation we found that phthalanilic acid could be easily prepared from its constituents without the use of a solvent. Phthalic acid, 10 grams, and aniline, 14.6 grams = about 2.25 mol., were mixed and allowed to remain at the ordinary temperature for 22 minutes. The flask was found to have become hot and steam had condensed in its upper portion; moreover, the mixture had become very stiff. More aniline, 6.7 grams, was now added and the substance heated on a boiling water-bath. After 7 minutes a portion was removed, washed with cold alcohol and recrystallized from more alcohol. At first the solution was pink, but it became yellow as the heating continued. The product melted at about 160°, resolidified and melted again at 190°–195°; it contained a considerable proportion of nitrogen, as shown by the sodium test. A portion which had been washed, but not recrystallized, behaved in a similar manner. The heating was continued for 4 hours on the water-bath and another portion withdrawn; after purification in the manner described it gave the same results. A further 5 hours' heating, 9 hours altogether, gave a product which was chiefly phthalanilic acid, but the alcoholic washings, containing, of course, the excess of aniline, after standing for a time at the ordinary temperature, deposited phthalanil. This is certainly the easiest method known to us for making phthalanilic acid and the yield appeared to be very good. We did not investigate the matter further because we had already obtained as much of the acid as we required. We refer later (p. 601) to the readiness with which phthalanil is formed from phthalanilic acid in the presence of an excess of aniline.

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[1] *Loc. cit.*

[2] Ann. Chem. (Liebig), 210, 267 (1881.)

PHTHALANILIC ACID was obtained, without difficulty, from phthalanil by the method of Zincke and Cooksey,[1] which consists in treating the phthalanil with alcoholic potassium hydroxide and acidifying the resulting potassium salt. Our product melted at 164°, resolidified and melted again at 204°, showing that at its melting point this acid is changed into phthalanil. The yield was 25.5 grams of acid from 73 grams of phthalanil.

We carried out a considerable number of experiments with aniline and phthalic and phthalanilic acids, respectively, with the object of preparing PHTHALANILIDE, either in the manner employed for obtaining succinanilide (*vide* p. 597), or directly from the constituents. It was quickly evident that the anilide is, relatively, highly unstable and, like the anilic acid, is very readily transformed into the anil. We tried careful regulation of the temperature, with and without the use of aniline in excess. We obtained the phthalanilide in several experiments, but on repeating them it became manifest that this result was dependent on conditions beyond ordinary control and, consequently, we cannot regard the problem as being solved at all to our satisfaction. We give below a brief description of our experiments. In the preparation of phthalanil by the method of Zincke and Cooksey,[1] we separated the products of the reaction by means of sodium carbonate. On acidification a white precipitate was formed consisting, presumably, of phthalic and phthalanilic acids (*vide* p. 599). This mixture was added to enough aniline to form a stiff paste and heated on a water-bath for about 2 weeks. A portion of the product, washed twice wth cold dilute hydrochloric acid and then recrystallized from alcohol, melted at 230°, which is 1° below the melting point of phthalanilide. The remainder of the aniline mixture was now heated at 140° for 3 or 4 days, and was then found to consist of phthalanil.

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[1] Ann. Chem. (Liebig), **255**, 375 (1889).

In another experiment, phthalic acid, 9 grams, and aniline, 22 grams, were heated on the water-bath for 2 days. The product was purified by means of hydrochloric acid and alcohol, as described above, and melted at 215°–220°. The melting points of phthalanil and of phthalic acid are 203° and 213°, respectively. Boiling for 6 hours with alcohol, or prolonged heating on the water-bath with an additional quantity of aniline caused no change in the melting point of the product. A further 5 grams of aniline were now added and the mixture heated at 120°–130°, for 1.5 days. The product melted at 201°–205°, showing it to be, essentially, phthalanil.

Phthalanilic acid, 5 grams, and aniline, 12.5 grams, were heated at 120°–310°, for 1.5 days; the product melted at about 201° and further heating of the mixture at 140°–190° produced no decided change in this respect. Additional experiments were made with similar mixtures of phthalanilic acid and aniline, at temperatures ranging from that of the room up to the one given by a boiling water-bath. In some cases the product was recrystallized from alcohol, in others washed with cold alcohol, or with cold hydrochloric acid. The substances obtained consisted either wholly of phthalanil, or of mixtures of this with phthalanilic acid; moreover, we found that boiling the alcoholic washings, containing aniline and phthalanilic acid, always resulted in the formation of phthalanil.

A similar series of experiments was carried out with phthalic acid and aniline, but we failed to obtain any of the anilide.

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[1] *Loc. cit.*

We found, however, that phthalanilic acid, as already stated, is easily prepared by simply mixing phthalic acid, 1 mol., with aniline, 2.5 mol., at the ordinary temperature.

We think our results indicate that, although the formation of succinanilic acid and of phthalanilic acid take place in a similar manner, yet in the presence of aniline the further reaction of these substances is quite different, the former yielding succinanilide and the latter phthalanil; moreover, this difference is not by any means simply a question of relative stability at a given temperature, because, as our experiments show, phthalanilic acid is more unstable at the temperature of a boiling water-bath, in the presence of a large excess of aniline, than in its absence. One experiment in support of this has already been given (p. 601) and 2 others may be cited. Phthalic acid, 10 grams, was mixed with aniline, 14.6 grams = about 2.25 mol., and, as it became thick more aniline, 6.7 grams, was added and the mixture heated in an open flask, on the water-bath, for 10 hours. After being washed with cold alcohol the solid residue was found to consist of phthalanilic acid. The alcoholic washings containing the aniline, without any further heating, soon deposited phthalanil. During a further 5 hours' heating the contents of the flask were accidentally allowed to become dry, as the excess of aniline is readily volatile in the steam formed during the reaction. The product was still phthalanilic acid. It was now moistened with aniline, allowed to remain at the ordinary temperature over Sunday, and then heated on the water-bath for a working day (8 hours). This treatment converted it completely into phthalanil.

The second experiment, illustrating the same point, is as follows: Phthalanilic acid, 3 grams, was mixed with enough aniline to form a thick paste and heated on a boiling water-bath for 2 minutes. A portion was removed, washed with cold alcohol and dried. It melted at about 145°, resolidified and then melted at about 200°, showing that it was unchanged phthalanilic acid. The alcoholic washings, after being concentrated, deposited phthalanil. The flask having been off the water-bath for 13 minutes, was now reheated for 2 minutes and a portion of the product tested. It behaved exactly like the first specimen. The flask having been off the bath for 12 minutes was now again heated for 6 minutes. The product was phthalanil. Eleven minutes' additional heating produced no further change. It may be mentioned that the solubility of phthalanil in alcohol is altogether too slight for it to have been removed from the product of the reaction by washing at the ordinary temperature and that it must, therefore, have been formed in the wash liquors. These experiments show that, whereas 15 hours' heating on the water-bath and one night's standing at the ordinary temperature is not sufficient to convert phthalanilic acid into phthalanil in the absence of excess of aniline, yet in the presence of such an excess the change is complete after 10 minutes' heating and 23 minutes' standing.

The phthalanilide which we required was finally prepared from aniline and phthalyl chloride, according to the method of Rogrow.[1] After recrystallization from alcohol it melted at 232°–233°, the temperature given in the literature being 231°.

The phthalyl chloride was obtained essentially according to the method of Claus and Hoch[2] and of Graebe.[3] Phthalic anhydride, 50 grams = 1 mol., was mixed with powdered phosphorus pentachloride, 70 grams = 1 mol., and heated in a reflux apparatus at 120°–170°, during 8 hours. Inadvertently, the temperature was allowed to rise for a short time to 210°. The phosphorus oxychloride was volatilized under the ordinary pressure and the residue distilled; it boiled at about 47° (130 mm.). After standing for an hour the distillate deposited crystals which were proved to consist of unchanged phthalic anhydride; they were removed by filtration and the liquid chloride gradually added to an alcoholic solution of aniline, in the manner indicated above. The yield of purified chloride was 22.6 grams and about 22 grams of unchanged phthalic anhydride were recovered. The above experimental conditions offer the great advantage of yielding a product which is, apparently, entirely free from chlorine substitution products isomeric with phthalyl chloride, and from phthalyl tetrachloride. These substances were encountered by the chemists mentioned above, and their separation caused a good deal of trouble and loss of material. We attribute our success chiefly to the distillation of the crude material under reduced pressure, and believe that the yield of phthalyl chloride could be improved by the use of a larger proportion of phosphorus pentachloride, without much danger of the formation of isomeric chlorine compounds. The work is being continued by one of us in conjunction with Mr. Lovelace.

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[1] Ber. d. chem. Ges., **30**, 1442 (1897.)

[2] *Ibid.*, **19**, 1187 (1886).

[3] Ann. Chem. (Liebig), **238**, 329 (1887).

JOHNS HOPKINS UNIVERSITY,
December, 1906.

A FORMALDEHYDE COLOR TEST FOR PROTEIDS. I.

BY S. F. ACREE.

[The writer is indebted to the Carnegie Institution of Washington for aid in this work.]

The biuret reaction was considered up to within the last 5 years to be the most reliable of the numerous color tests for the proteids. It was supposed that by this reaction we could differentiate the proteids from the decomposition products, as the former and only the former, with very few exceptions, always gave this color reaction. But concurrently with the synthesis of the large number of polypeptides by Emil Fischer, Theodor Curtius and their co-workers, it has been discovered that a very large number of these polypeptides give the biuret reaction fully as well as the complex proteids. Furthermore, it has recently been found that a number of substances that behave like peptones, and that are much more complicated than even the most complex synthetical polypeptides, do not give the biuret reaction.[1]

Since the reliability of this reaction has been so often questioned, the writer has been led to develop another color test for the proteids, in the hope that it might prove to be a more reliable reaction than the biuret test. The results have proved so satisfactory that a preliminary announcement is now made.

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[1] For a general discussion and references see Cohnheim, "Chem. d. Eiweisskörper," 1904, p. 61.

The writer hopes that others who are working with proteid substances or their decomposition products will apply this test and publish their results, so that we can learn just how far this particular color reaction is of value in attempting to decide if the given substance is a complex proteid.

It was found in the course of a study of the Hehner test for formic aldehyde in milk, that the casein and other proteid constituents are the substances that give the color test, and that several other proteids behave similarly;[1] that is, if a very small amount, about 0.01 gram, of casein or lactalbumin is mixed with 0.1 cc. of 1 : 5000 formic aldehyde solution and to this there is added 0.5 cc. of commercial concentrated sulphuric acid, a violet zone is formed between the sulphuric acid and the solution. The writer has seen statements in the literature that a few proteids give this color test, but so far as he is aware no work has been done to determine if the test is a general one for proteids. Other work on the relation of the concentration of the solutions to the intensity of the color is being done. It can be stated now that a concentrated solution of formic aldehyde must not be used, and that one of the concentration 1 : 5000 is very satisfactory. We are, furthermore, trying experiments with various other aldehydes, ketones, etc. The formic aldehyde must be allowed to react on the proteid first, and then the concentrated commercial sulphuric acid is added. If the acid is added to the proteid first, and then the formic aldehyde is added, the colored substance is not formed, or at best is formed only very slowly. If a check test with the same amounts of water, instead of the formic aldehyde solution, proteid and acid is made, no color is developed. Since formic aldehyde reacts very readily with proteids,[2] it is probable that the formic aldehyde-proteids react with the acid and give the colored compounds. The fact that when water is added to the mixture the color is not discharged makes it appear probable that the colored compounds are not colored carbinol salts,[3] but salts of bases with chromophore groups. The nature of these colored compounds will be made a subject of investigation.

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[1] Acree : J. Biol. Chem., **2**, 145.

[2] Blum : Z. physiol. Chem., **22**, 127 ; Schwartz : *Ibid.*, **31**, 460 ; Benedicenti : Arch. Anat. physiol., 1897, p. 217.

[3] Acree : Ber. d. chem. Ges., **37**, 626.

It is seen at once that this color test is so delicate that it would prove to be very valuable for detecting the presence of small quantities of proteids, provided that only proteids give the test. The reaction has been applied to a large number of substances of varying chemical character. It can be stated, in general, *that the formic aldehyde compound of every proteid tested gave a violet color, whereas, no other classes of substances gave this reaction.* In general, such substances as simple organic acids, sugars, alcohols, esters, amides, phenols, urazoles, semicarbazides, amino acids, polypeptides and cyclic nitrogen compounds do not give the slightest color. In a few cases some violet color was developed, but in the check experiments without the formic aldehyde the same color exactly was shown; this was never the case with the proteids tested, and this fact enables us to distinguish the proteids from the non-proteids, so far as tested. In other words, the formic aldehyde reaction, as far as tested, is much better than the biuret reaction for it enables us to differentiate complex proteids from such compounds as polypeptides, uric acid derivatives and pyrimidines.

One very important phase of the work will next be developed. Will this reaction enable us to distinguish the simpler proteids, such as the albumoses, peptones, etc., from the complex proteids or the very simple derivatives? We shall try to secure a large number of these simpler proteids and carry on this work. The writer will be greatly obliged if workers in these fields will send him samples of about 0.10 gram of any complex or simpler proteids on hand, or will make the tests and report them in the literature. It is very likely, of course, that many substances which must be classed between the proteids and the simpler decomposition products will give this color reaction.

The writer is much indebted to Professors Abel, Osborne, Curtius, Grindley, T. B. Johnson, W. Jones, R. Hunt, M. T. Bogert, A. S. Loevenhart, W. F. Koelker, P. A. Levene, Bardachzi, and others, for substances supplied for this work.

The compounds furnished by each are noted in the column "Source." Other compounds were bought in the market; those furnished by Bender & Hobein are marked "B. & H." in the "Source" column. It will be noted that, in a few instances, the same substance from different sources has been tabulated; this was done to see if the substance made by one method might, because of some impurity, give a color test different from that given by the same compound made by a different method. All samples of the same substance behaved alike.

The following table gives a list of the substances tested. In general, 0.01 gram of the substance was treated with 0.10 cc. of 1:5000 formic aldehyde for 2 or 3 minutes and to this was then added about 0.5 cc. of concentrated commercial sulphuric acid so that there were 2 layers. The proteids gave a violet colored zone between the 2 liquids. Check tests were made in many cases by treating 0.01 gram of substance with 0.10 cc. of water and 0.5 cc. of acid. The proteids never gave any color in the check tests, but a few other substances, noted in the tables below, gave colored compounds. The work will be continued. The writer is much indebted to Dr. R. F. Brunel for aid in this work.

SUPPLEMENTARY NOTE.

Since this article was written the writer has had access to the very interesting communication of Otto Rosenheim.[1] A preliminary announcement of this work was made in an article in the *Journal of Biological Chemistry*, August, 1906, which was presented to the editor on Feb. 26th, or some time before Rosenheim's article left his hands. Furthermore, since the writer has been studying this reaction for more than 2 years, as time and the acquisition of substances would permit, he feels that he has a perfect right to continue the work, and will do so along the lines outlined. Although Rosenheim believes the reaction to be a general one for proteids, he does not give any experimental evidence, as the writer does, to show that it is characteristic of proteids and not of non-proteids.

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[1] Bio.-Chem. J., 1, 233.

Rosenheim's work is very interesting in that he thinks it probable that the tryptophan (indole) group is the basis of the color changes, as is the case with the Adamkiewicz reaction. It should be pointed out, however, that Konto[1] has shown that indole alone gives the test. Perhaps other groups may be concerned, or give the color entirely independently of tryptophan. Only the isolation and thorough study of the colored substance, or substances, can give the evidence needed to clear up the question. A sample of tryptophan kindly furnished by Dr. P. A. Levene gave a reddish-violet color, and a faint green color in the check test. A sample of the same substance, for which I am indebted to Bardachzi, gave a violet color with much more red than the sample prepared by Levene, but the check test gave the same light green color. The tryptophan is inserted in the list of proteids merely for comparison. Although the writer had intended to take up these reactions, he will not interfere with Rosenheim's work, but the writer cannot wholly agree with Rosenheim in regard to the mechanism of the reaction. Rosenheim believes (p. 234) that the reaction may take place in either one of two ways: (1) The formic aldehyde is oxidized first, giving rise to an intermediate oxidation product which reacts with the proteid, or (2) the formic aldehyde may combine with the proteid first, the resulting aldehyde-proteid compound being subsequently oxidized. Rosenheim believes that (1) is a possible explanation because an aqueous suspension of ammonium compound of diformic aldehyde peroxide hydrate was found to give the characteristic color with the proteid and sulphuric acid. The writer believes that all the experimental evidence now at hand excludes (1) and points to (2) as the course of the reaction. In the first place, the writer has never been able to get the color test well if the aldehyde-proteid compound was not formed first; if the proteid is added to the acid first and the formic aldehyde is added afterwards the color appears very slowly; the acid probably polymerizes the formic aldehyde and acts upon the proteid so that the formic aldehyde-proteid compound cannot be formed. The reason is not clear. If some such intermediate oxidation product of formic aldehyde is really first formed according to (1), as the test is usually made, and if it then reacts with the proteid in the presence of the acid, it is not apparent why such a series of reactions should not take place readily when the acid is added to the proteid before the formic aldehyde is added. It might be objected by Rosenheim that the oxidizing agent present in the acid is used up by the proteid when the proteid is first added to the acid, and that there is no oxidizing agent present then to act upon the formic aldehyde when it is added. This objection is met by the fact that when a mixture of the commercial acid and globulin from squash-seed are treated with the formic aldehyde the color appears very slowly. But when this very same proteid-sulphuric acid solution is added to some of the proteid-formic aldehyde compound the colored substance is formed at once. The formation of the color test by the use of ammonium compound of diformic aldehyde peroxide hydrate is just what we should expect from (2). The compound is probably hydrolyzed to some extent in water[1] into ammonia, hydrogen peroxide and formic aldehyde; the formic aldehyde then reacts with the proteid, and, when the sulphuric acid is added, the necessary constituents, the formic aldehyde-proteid and the hydrogen peroxide, are present to give the color test. It seems then that all the evidence is in favor of explanation (2), the one pointed out by the writer in this article.

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[1] Z. physiol. Chem., 48, 185.

Rosenheim states that the gelatin used by him gave no color test. The commercial gelatin used in this laboratory gave the color test slowly, but the writer cannot vouch for the quality of this material. Furthermore, since the samples of gelatoses furnished by Levene also gave faint color tests, it seems probable that there is present some constituent in gelatin which really gives the color test. This may be a very small trace of tryptophan or some other constituent. It is well known that gelatin certainly does not contain very much tryptophan.

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[1] Baeyer and Villiger: Ber. d. chem. Ges., **33**, 2479. Nef: Ann. Chem. (Liebig), **298**, 293.

EXPERIMENTAL PART.

PROTEIDS.

	Substance.	Color.	Check test.	Source.
1	Legumin—horse bean	Violet at once	No color	Osborne
2	Conglutin—yellow lupine	Violet slowly	"	"
3	Ovalbumin (very pure) hen's egg	Violet at once	"	"
4	Vignin—cow pea	Violet slowly	"	"
5	Globulin—cotton seed	Violet quickly	"	"
6	Hardein—barley	Violet at once	"	"
7	Amandin—almonds	" " "	"	"
8	Gliadin—rye	" " "	"	"
9	Novitellin—hen's egg	" " "	"	"
10	Globulin—castor bean	" " "	"	"
11	Inglansen—English walnut	" " "	"	"
12	Glycinin—soy bean	Violet quickly	"	"
13	Excelsin—brazil nut	Violet at once		
14	Globulin—squash seed	Deep violet at once	"	"
15	Edestin—hemp seed	Violet at once	"	"
16	Gliadin—wheat	" " "	"	"
17	Glutenin	" " "	"	"
18	Phaseolin—kidney bean	" " "	"	"
19	Protein—flour	" " "	"	Acree
20	Casein	" " "	"	Casein Co. of America
21	Nucleo-casein	" " "	"	Casein Co. of America

PROTEIDS.—*Continued.*

	Substance.	Color.	Check test.	Source.
22	Milcora from skim milk	Violet at once	No color	Casein Co. of America
23	Albumose	" " "	"	Grindley
24	Coagulum (60°) from water extract of beef	Fine violet at once	"	"
25	Lima bean	Violet at once	"	Acree
26	Saliva	Violet slowly	"	"
27	Keratin	Violet at once	"	Abel
28	Ossein	Violet slowly	"	"
29	Casein—commercial	Violet at once	"	
30	Paracasein	" " "	"	Loevenhart
31	Gelatine—commercial	Violet slowly	"	
32	Beef	Violet at once	"	
33	Milk	" " "	"	
34	White of hen's egg (fresh)	" " "	"	
35	Fish albumin—commercial	" " "	"	
36	Pepsin—commercial	Blue-violet at once	"	
37	Prototryptogelatose	Faint violet-red	Reddish	Levene
38	Deuterotryptogelatose	" " "	"	"
39	I peptone	Red-violet	"	"
40	Mannonucleic acid	Charred	Charred	"
41	Tryptophan	Red-violet	Faint green	"
42	Tryptophan	Red-violet, with more red than with No. 41	" "	Bardachzi

NON-PROTEID SUBSTANCES.

Amino Acids and Polypeptides.

	Substance.	Color.	Check test.	Source.
1	Glycocoll	No color	———	Koelker
2	Leucine nitrate	“	No color	“
3	Asparaginic acid	“	“	“
4	Hippurylalanine	“	“	“
5	Hippurylasparaginic acid	“	“	“
6	Hippurylalanylalanine	“	“	“
7	Hippurylisoserine	“	“	“
8	Tryosine	“	“	“
9	Leucylisoserine	“	“	“
10	Leucylisoserine (B)	“	“	“
11	α-Bromisocapronylisoserine	“	“	“
12	Alanine	“	“	“
13	Benzoylpentaglycylglycine	“	“	“
14	Asparagine	“	“	B. & H.
15	Glycocoll	“	“	“
16	Leucine	Brown	Brown	“
17	Alanine	No color	———	“
18	Taurine	“	———	“
19	Sarcosine	“	———	“
20	Sarcosine	“	———	Kahlbaum
21	Aspartic acid	“	No color	Levene
22	Glutaminic acid	“	“	“
23	Oxyprolein	Light yellow	Light yellow	“
24	α-Prolein	No color	No color	“

NON-PROTEID SUBSTANCES.—*Continued.*

Amides, Ureas, Semicarbazides, Hydrazines.

	Substance.	Color.	Check test.	Source.
25	Triphenylguanidine	No color	No color	Acree
26	1-Phenylthiosemicarbazide	Pink	Deep green	“
27	Semicarbazide hydrochloride	No color	No color	“
28	Phenylsemicarbazide	Deep red	Deep red	“
29	Formamide	No color	No color	B. & H.
30	Acetamide	“	“	“
31	Asparagine	“	“	“
32	Succinimide	“	“	“
33	Succinamide	“	“	“
34	Oxamide	“	“	“
35	Cyanamide	“	“	“
36	Urethane	“	“	“
37	Biuret	“	“	“
38	Thiourea	“	———	“
39	Urea	“	———	“
40	Phenylurea	“	———	“
41	Amidoguanidine nitrate	Violet	Violet	“
42	Phenylurethane	No color	———	“
43	Thiocarbanilide	“	———	“
44	Benzylidinephenylhydrazine	“	———	“
45	Phenacetin	“	———	“
46	*p*-Aminoazobenzene	Red color	Red color	“
47	Acetanilide	No color	———	“

NON-PROTEID SUBSTANCES.—*Continued.*

Amides, Ureas, Semicarbazides, Hydrazines.—Continued.

	Substance.	Color.	Check test.	Source.
48	Amygdalin	Color changing from bright purple at first to a pink	Color changing from bright purple at first to a pink	B. & H.
49	Benzamide	No color	———	“
50	Diazoaminobenzene	Dark brown	Dark brown	“
51	*m*-Aminophenol	“ “	“ “	“
52	Saccharin	No color	———	“
	Saccharin	“	———	Remsen
53	Carbazole	Light green	Light green	B. & H.
54	Triethylamine	No color	———	“
55	Methylacetanilide	“	———	“
56	Methylamine hydrochloride	“	———	“
57	Cyanacetic acid	“	———	“
58	Xylenesulphonamide	“	———	“

Cyclic Nitrogen Compounds.

	Substance.	Color.	Check test.	Source.
59	1-Phenyl-4-methylurazole	No color	No color	Acree
60	1-Phenyl-3-thio-4-methylurazole	“	“	“
61	1-Phenylurazole	“	“	“
62	Xanthine nitrate	“	“	W. Jones
63	Alloxan	“	“	Kahlbaum

Cyclic Nitrogen Compounds.—Continued.

	Substance.	Color.	Check test.	Source.
64	Chitin	No color	No color	Abel
65	Guanine hydrochloride	"	"	W. Jones
66	Uracil	"	"	Johnson
67	Cytosine	"	"	"
68	Thymine	Red color	"	"
69	5-Amino-4-oxyquinazoline	Pink color	Pink color	Bogert
70	2-Methyl-4-oxyquinazoline	No color	No color	"
71	Uric acid	"	"	B. & H.
72	Barbituric acid	"	"	"
73	Alloxantine	"	"	"
74	Theobromine	"	———	"
75	Caffeine	"	———	"
76	Cyanuric acid	"	———	"
77	Murexid	Violet	Violet	"
78	Creatine	No color	———	"
79	Cyamelide	"	———	"
80	Paracyanogen	"	———	"
81	Alloxantine	"	———	"
82	Peptone	"	———	Grindley and Trowbridge
83	Antipyrin	"	———	Kahlbaum
84	Carbazole	Light green	Light green	"
85	Isatin	Dark brown	Dark brown	"
86	Brucine sulphate	No color	———	B. & H.
87	Strychnine	"	———	"

NON-PROTEID SUBSTANCES.—*Continued.*

Cyclic Nitrogen Compounds.—Continued.

	Substance.	Color.	Check test.	Source.
88	Cocaine	No color	———	B. & H.
89	Takadiastase	Brown	———	"
90	Piperine	Dark brown	Dark brown	"
91	Opium	Charred	Charred	"
92	Morphine sulphate	Light purple	Light purple	"
93	Codeine	" "	" "	"
94	Haemoglobin	No color	———	"
95	Haematin	"	———	"
96	Quinine sulphate	"	———	"
97	Quinidine	"	———	"
98	Ethyl dihydrocollidinedicarboxylate	"	———	"
99	Haematein	Dark red, with charring	Dark red, with charring	"
100	Pyridine	Light purple	Light purple	"
101	Lutidine	" "	" "	"
102	Diastase	Brown	Brown	"
103	Nicotine	"	———	"
104	Quinoline	No color	———	"
105	Quinaldine	"	———	"

Sugars and Esters.

	Substance.	Color.	Check test.	Source.
106	Glucose	No color	No color	B. & H.
107	Cane sugar	"	"	"
108	Lactose	"	"	"

NON-PROTEID SUBSTANCES.—*Continued.*

Sugars and Esters.—Continued.

	Substance.	Color.	Check test.	Source.
109	Butter fat	No color	No color	B. & H.
110	Lard	"	"	"
111	Galactose	"	———	"
112	Mannite	"	———	"
113	Dextrin	Dark brown	Dark brown	"
114	Glucovanillin	Charred	Charred	"
115	Creosote oleate	Light brown	Light brown	"
116	Starch	No color	No color	"
117	Lanolin	Brown-red	Brown-red	"
118	Salicin	Purple	Purple	"
119	Coniferin	"	"	"
	Saccharin (*vide* 4)			

Acids and Phenols.

	Substance.	Color.	Check test.	Source.
120	Glycocholic acid	Dark green, changing to purple	Dark green, changing to purple	B. & H.
121	Thymol	Light red	Light red	"
122	Gallic acid	No color	———	"
123	Tannic acid	"	———	"
124	Alizarin	Dark red	Dark red	"
125	Margaric acid	No color	———	"
126	Sebacic acid	"	———	"
127	Hydroquinol	Purple	Purple	"
128	Malic acid	No color	———	"

NON-PROTEID SUBSTANCES.—*Continued.*

Miscellaneous.

	Substance.	Color.	Check test.	Source.
129	Potassium xanthogenate	No color	———	B. & H.
130	Stilbene	"	———	"
131	Phenanthrene	"	———	"
132	Apolysin	"	———	"
133	Solveol	"	———	"
134	Hexachlorethane	"	———	"
135	*m*-Chlornitrobenzene	Purple	Purple	"
136	Ionone	Dark brown	Dark brown	"

It was pointed out in the preliminary notice that other aldehydes had been worked with and that vanillin gives the violet color with proteids very nicely.

The writer will continue the work outlined in this article, but will try not to interfere with Rosenheim's work.

JOHNS HOPKINS UNIVERSITY,
July 1, 1906.

THE DETERMINATION OF TRANSITION TEMPERATURES.

BY DAVID W. HORN.

The object of this paper is to describe a simple method of determining transition temperatures in systems of the second order, consisting of 2 solid phases and a vapor phase. The method is applicable to *dissociation* in systems where 1 of the 2 components has a negligible vapor pressure, while the other component, under the same conditions, constitutes the vapor phase. The method, slightly modified, can be used at different pressures, and in many cases can supply the information heretofore obtained by the far more laborious measurements of vapor pressures.

The time required for a determination ranges from 45 to 90 minutes; it may be reduced to a fraction of that time by using less of the dissociating solid. The amount of substance necessary is very small indeed. The apparatus used in the 4 determinations given in this paper consisted of a thermometer, a small clock with a second hand, and a test tube, supplemented, in some cases, by a filter pump and a water-bath.

The test tube had an internal diameter of about 1.8 cm. and a length of 12 cm. It was closed by a rubber stopper with 2 perforations. Through one of them a thermometer was passed so that its bulb was in the lower end of the test tube when the stopper was in place. In the bottom of the test tube and about the bulb of the thermometer was placed the solid whose temperature of dissociation was to be determined. Through the second perforation in the stopper a delivery tube passed. This delivery tube was bent in such a way that its outer end could be placed beneath a surface of mercury while the test tube and thermometer occupied an almost vertical position. This arrangement was used when ammonia was the vapor evolved in the dissociation. When water was evolved, the delivery tube was attached to a filter pump. The apparatus can readily be modified to fit other cases. When the delivery tube is lengthened and graduated, pressures considerably above 1 atmosphere can be obtained by inserting the delivery tube in a somewhat wider tube of suitable length containing mercury. Other modifications readily suggest themselves.

I first used the method to locate the temperatures at which higher and unstable cuprammonium compounds decompose into ammonia and simpler and more stable cuprammonium compounds. Borax was then examined as an instance of a dissociating hydrated salt. Sodium bicarbonate was taken to illustrate dissociation when the vapor phase contains more than 1 molecular species. Finally, as a check upon the method, the transition-temperature of the compound $AgCl.3NH_3$ was determined. This substance was selected because the transition temperature can also be obtained by plotting the values for the tensions of ammonia over this compound at different temperatures obtained by Isambert[1] and by Horstmann.[2] A second reason for selecting this substance was that the transition takes place near 20°, the room temperature, where errors due to the exposed stem of the thermometer and other errors affecting its reading are less significant.

The data are given in the tables that follow. The curves plotted from these tables have the same general form as inverted "cooling curves." The horizontal portions represent the transition temperatures, just as the horizontal portions of cooling curves represent freezing points. The methods of obtaining the data and of using it are so simple that they require no discussion beyond that found in the necessary explanations accompanying each of the following experiments.

EXPERIMENT I.

Cuprammonium Nitrate.

The solid examined was a deep blue, crystalline substance obtained when the solvent, liquid ammonia, had evaporated from a solution made by dissolving the compound,

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[1] Ann. Ecol. Norm., **5**, 129 (1868).

[2] Ber. d. chem. Ges., **9**, 756 (1876).

$$Cu(NO_3)_2.4NH_3.$$

As the substance warms to room temperature its color changes from blue to lilac, and ammonia is evolved. The dissociation takes place as follows:

$$Cu(NO_3)_2.5NH_3 \rightleftarrows Cu(NO_3)_2.4NH_3 + NH_3.$$

The blue nitrate will be discussed in detail along with some other new cuprammonium salts in a separate paper

The air, at about 20°, served as the constant temperature bath. The thermometer used had a scale length of 21.6 cm., and was graduated from —14° to +32°, into tenths. It was read every minute. The time was read from the second hand of a small clock. The readings were continued for 1¼ hours.

The transition temperature was registered by the thermometer between 15°.29 and 15°.31. The reading of the thermometer was practically constant for more than 15 minutes.

EXPERIMENT II.

Borax.

The solid examined was taken directly from the stock bottle in the laboratory, finely ground in a porcelain mortar, and introduced into the test tube in sufficient quantity to cover the bulb of the thermometer. The dissociation takes place as follows:

$$Na_2B_4O_7.10H_2O \rightleftarrows 5H_2O + Na_2B_4O_7.5H_2O.$$

A water-bath stirred by hand was used. Its temperature was maintained between 69° and 69°.6 The thermometer employed had a scale length of 38 cm. and was graduated from —3° to +60° into tenths. It was read every half minute for about ¾ hour. The delivery tube was connected with an efficient filter pump, which was kept in constant action. This was done because borax, like most other salts

Table I.—Cuprammonium Nitrate.

Time. Minutes.	Temperatures.	Time. Minutes.	Temperatures.	Time. Minutes.	Temperatures.	Time. Minutes.	Temperatures.
0	7°.3	24	16°.39	48	15°.32	73	16°.51
1	8°.5	25	16°.31	49	15°.32	74¼	16.°65
2	9°.7	26	16°.27	50	15°.32		
3	10°.9	27	16°.21	51	15°.30		
4	11°.9	28	16°.19	52	15°.30		
5	12°.8	29	16°.10	53	15°.30		
6	13°.57	30	16°.01	54	15°.30		
7	14°.25	31	15°.96	55	15°.30		
8	14°.90	32	15°.89	56	15°.29		
9	15°.48	33	15°.83	57	15°.29		
10	16°.00	34	15°.77	58	15°.30		
11	16°.40	35	15°.72	59	15°.30		
12	16°.80	36	15°.69	60	15°.30		
13	17°.03	37	15°.62	61	15°.30		
14	17°.20	38	15°.52	62	15°.30		
15	17°.28	39	15°.50	63	15°.33		
16	17°.29	40	15°.49	64	15°.40		
17	17°.19	41	15°.43	65	15°.50		
18	17°.04	42	15°.41	66	15°.60		
19	16°.90	43	15°.40	67	15°.67		
20	16°.78	44	15°.37	68	15°.82		
21	16°.63	45	15°.33	69	15°.99		
22	16°.53	46	15°.30	70	16°.13		
23	16°.48	47	15°.30	71	16°.30		

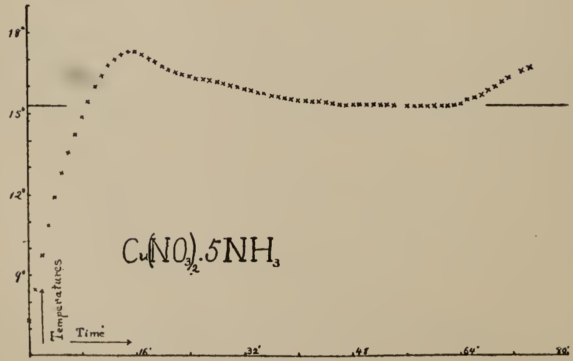

Fig. I.

with water of crystallization, does not exhibit a dissociation pressure equal to 1 atmosphere while the temperature is below 100°. No condensation of the water vapor evolved occurred within the apparatus. When the pump is stopped at the close of the experiment the dissociation is immediately slowed up, and the temperature once more rises very suddenly. The transition temperature registered by the thermometer was 47°.42 to 47°.47 and was maintained practically constant during 7 minutes.

Table II.—Borax.

Time. Minutes.	Temperature.	Time. Minutes.	Temperature.	Time. Minutes.	Temperature.	Time. Minutes.	Temperature.
		11½	47°.86	23½	47°.46	35½	48°.71
0	42°.9	12	47°.82	24	47°.49	36	48°.80
½	44°.3	12½	47°.75	24½	47°.50	36½	48°.87
1	45°.23	13	47°.70	25	47°.50	37	48°.95
1½	46°.2	13½	47°.67	25½	47°.55	37½	49°.02
2	46°.82	14	47°.60	26	47°.60	38	49°.12
2½	47°.30	14½	47°.60	26½	47°.63	38½	49°.18
3	47°.66	15	47°.58	27	47°.69	39	49°.27
3½	47°.92	15½	47°.54	27½	47°.75	39½	49°.37
4	48°.11	16	47°.51	28	47°.80	40	49°.42
4½	48°.25	16½	47°.50	28½	47°.85	41	49°.57
5	48°.30	17	47°.50	29	47°.90	42	49°.68
5½	48°.31	17½	47°.47	29½	47°.99		
6	48°.35	18	47°.47	30	48°.07		
6½	48°.35	18½	47°.46	30½	48°.11		
7	48°.35	19	47°.46	31	48°.16		
7½	48°.35	19½	47°.42	31½	48°.22		
8	48°.25	20	47°.42	32	48°.29		
8½	48°.20	20½	47°.42	32½	48°.35		
9	48°.17	21	47°.46	33	48°.40		
9½	48°.11	21½	47°.47	33½	48°.45		
10	48°.07	22	47°.47	34	48°.51		
10½	48°.00	22½	47°.45	34½	48°.59		
11	47°.94	23	47°.45	35	48°.64		

EXPERIMENT III.

Sodium Bicarbonate.

The solid examined was taken from the laboratory stock. It was not further pulverized. The dissociation takes place as follows:

$$2NaHCO_3 \rightleftharpoons Na_2CO_3 + H_2O + CO_2.$$

A bath of boiling water was used. The thermometer had a scale length of 30.5 cm. and was graduated from 46° to 106°, in tenths. It was read every half minute for about 45 minutes. The filter pump was used continuously as in Experiment II.

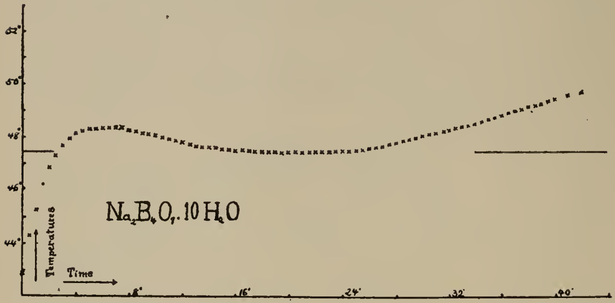

Fig. II.

The transition temperature registered was 90°.80 to 90°.88. The temperatures remained within these limits about 12 minutes.

EXPERIMENT IV.

Ammonia Silver Chloride.

The solid examined was made from precipitated silver chloride, the precipitate being prepared by pouring hot dilute potassium chloride solution very slowly into a slight excess of hot dilute silver nitrate solution. The precipitate was repeatedly washed with hot water by violently shaking it in a flask with the water in such a way as to break up the clots. The precipitate was collected and placed in a press between pads of filter paper. When as much water had been removed as possible by this method, the precipitate was finely ground and placed, for 24 hours, in a desiccator over sulphuric acid. Before it was used it was heated on

Table III.—Sodium Bicarbonate.

Time minutes.	Temperature.	Time minutes.	Temperature.	Time minutes.	Temperature.	Time minutes.	Temperature.
0	82°.7	8½	93°.00	21	90°.89	33	90°.90
¼	83°.5	9	92°.91	21½	90°.88	33½	90°.90
½	84°.2	9½	92°.80	22	90°.87	34	90°.91
¾	84°.9	10	92°.70	22½	90°.85	34½	90°.92
1	85°.6	10½	92°.55	23	90°.83	35	90°.97
1¼	86°.2	11	92°.41	23½	90°.81	35½	90°.99
1½	86°.9	11½	92°.27	24	90°.80	36	91°.01
1¾	87°.6	12	92°.15	24½	90°.81	36½	91°.01
2	88°.2	12½	92°.02	25	90°.81	37	91°.02
2¼	88°.7	13	91°.90	25½	90°.81	37½	91°.02
2½	89°.3	13½	91°.80	26	90°.81	38	91°.03
2¾	89°.8	14	91°.70	26½	90°.81	38½	91°.05
3	90°.2	14½	91°.59	27	90°.81	39	91°.09
3¼	90°.6	15	91°.50	27½	90°.83	39½	91°.10
3½	90°.95	15½	91°.40	28	90°.84	40	91°.11
3¾	91°.30	16	91°.33	28½	90°.86	40½	91°.12
4	91°.60	16½	91°.28	29	90°.86	41	91°.13
4½	92°.05	17	91°.21	29½	90°.86	42	91°.13
5	92°.48	17½	91°.14	30	90°.86	43	91°.19
5½	92°.73	18	91°.10	30½	90°.86	44	91°.20
6	92°.91	18½	91°.05	31	90°.86	45	91°.28
6½	93°.04	19	91°.00	31½	90°.88	46	91°.38
7	93°.10	19½	90°.96	32	90°.88	47	91°.48
7½	93°.10	20	90°.93	32½	90°.89	48	91°.56
8	93°.09	20½	90°.90				

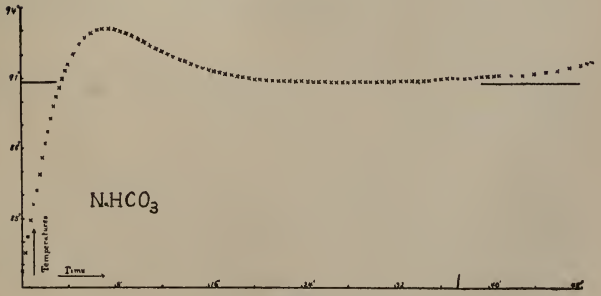

Fig. III.

glass 4 hours at 100°. All of these operations were carried out in the dark. When light was necessary, an electric incandescent lamp, encased in 2 thicknesses of heavy paper was used.

Enough of the dry chloride to cover the bulb of the thermometer was introduced into the test tube, which was protected from light by a movable black paper jacket. Liquid ammonia was drawn upon the chloride until it was completely submerged. After the liquid ammonia had boiled off, the test tube was introduced into a water thermostat at 24°.5. The readings were made every ¼ minute, but only some of the readings are given in the table, as the rest were unnecessary for plotting the curve. The thermometer used was the same as in Experiment II.

The transition temperature registered was 19°.39, and not the slightest deviation in the reading of the thermometer could be observed for over 0.5 hour.

After the experiments had been completed the thermometers were corrected. Each thermometer was compared with a standard thermometer when both were immersed in a water-bath at a temperature identical with the transition temperature which the uncorrected thermometer had been used to measure. The standard thermometer was graduated into fifths and had been corrected to 0°.1 degree in September, 1906, by the Physikalisch-Technische Reichsanstalt (PTR 27863). In the following table the corrected transition temperatures are given:

Cuprammonium nitrate	15°.30–15°.32	at	approx.	76	cm.	pres.
Borax	47°.9 –48°.0	"	"	2	"	"
Sodium bicarbonate	90°.4 –90°.48	"	"	2	"	"
Ammoniosilver chloride	19°.4	"	"	76	"	"

The last value, as stated, was determined as a test of the method. From Isambert's curve of vapor pressures this temperature should be 19°.9; from Horstmann's, 19°.05; the average of the two is 19°.47. Therefore, the reliability of the method proposed in this paper is certainly within the limits of error in the older vapor pressure method.

Table IV.—Ammonia Silver Chloride.

Time minutes.	Temperature.	Time minutes.	Temperature.	Time minutes.	Temperature.	Time minutes.	Temperature.
0	6°.9	10½	20°.35	24	19°.59	68	19°.39
½	9°.1	11	20°.35	25	19°.55	70	19°.41
1	11°.1	11½	20°.32	26	19°.53	72½	19°.43
1½	12°.7	12	20°.30	27	19°.51	74½	19°.45
2	14°.0	12½	20°.28	28	19°.50	77	19°.49
2½	15°.2	13	20°.22	29	19°.50	79½	19°.51
3	16°.2	13½	20°.19	30	19°.50	82	19°.51
3½	17°.0	14	20°.15	31	19°.49	85½	19°.53
4	17°.65	14½	21°.10	32	19°.45	88½	19°.58
4½	18°.20	15	21°.07	33	19°.44	91½	19°.60
5	18°.70	15½	20°.01	34	19°.42	93½	19°.62
5½	19°.10	16	19°.99	35	19°.41	96	19°.66
6	19°.40	16½	19°.92	36	19°.40	98	19°.71
6½	19°.65	17	19°.89	37	19°.40	102½	19°.75
7	19°.86	17½	19°.86	38	19°.39	104	19°.79
7½	20°.02	18	19°.83	43	19°.39	107	19°.81
8	20°.14	19	19°.78	48	19°.39	116	19°.99
8½	20°.21	20	19°.71	53	19°.39	132	20°.28
9	20°.30	21	19°.69	58	19°.39	142	20°.59
9½	20°.32	22	19°.63	63	19°.39	158	20°.74
10	20°.35	23	19°.60				

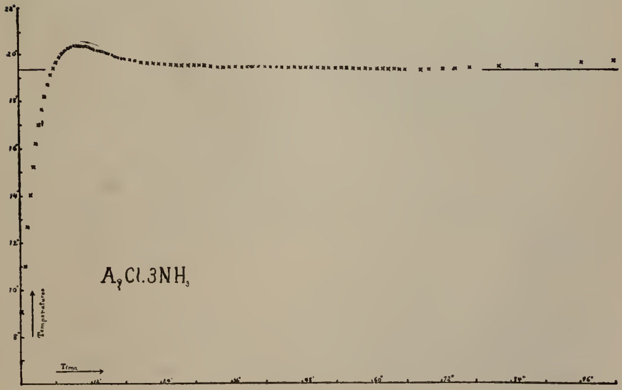

Fig. IV.

The transition temperatures of other solids that absorb heat when they dissociate are under investigation. The method is readily applicable to hydrated salts, ammonia compounds, addition products where the addenda are hydrochloric acid, hydrogen peroxide, hydrogen sulphide, alcohol, ether, benzene, organic bases, etc., as well as to the dissociable compounds like nitrates, carbonates and similar substances. It is applicable to systems of higher orders, such as

$$\mathrm{PbO + NH_4Cl \rightleftarrows Pb(OH)Cl + NH_3}.$$

Contributions from the Sheffield Laboratory of Yale University.

CXLIV.—RESEARCHES ON PYRIMIDINES: SOME CONDENSATION PRODUCTS OF A SUBSTITUTED PSEUDOTHIOUREA: SYNTHESIS OF 1-METHYLURACIL.

By Treat B. Johnson and F. W. Heyl.

(TWENTIETH PAPER.)

Substituted ureas apparently do not condense with β-ketone esters to form pyrimidines. While urea reacted with ethyl acetoacetate to form 4-methyluracil, II., Behrend[1] obtained no condensation products corresponding to methyluracil when phenylurea, diphenylurea and dimethylurea were treated with this ketone ester.

The alkyl derivatives of 4-methyluracil, II., in which the alkyl groups are linked to nitrogen, have all been prepared by heating this pyrimidine with alkyl halides[2] in presence of alkalis, or by condensing β-alkyluraminocrotonic esters, III., to pyrimidines, by treatment with alkali.[3] The corresponding alkyl derivatives of uracil, I., have not been described.

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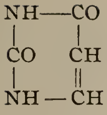
[1] Ann. Chem. (Liebig), **229**, 15; **233**, 1.

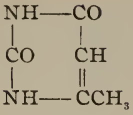
[1] Behrend : Ann. Chem. (Liebig), **229**, 23; **231**, 256; **253**, 67. Hagen : *Ibid.*, **244**, 2. Hoffman: *Ibid.*, **253**, 73. Behrend and Dietrich : *Ibid.*, **309**, 260. Behrend and Meyer : Ber. d. chem. Ges., **33**, 624.

[3] Behrend and Meyer : Ber. d. chem. Ges., **33**, 621. Behrend and Buchholz : Ann. Chem. (Liebig), **314**, 209. Behrend and Thurm : *Ibid.*, **323**, 160. Behrend and Hesse: *Ibid.*, **329**, 341.



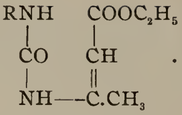
$$\begin{array}{lcl} \mathrm{NH} & \text{—} & \mathrm{CO} \\ | & & | \\ \mathrm{CO} & & \mathrm{CH} \\ | & & \| \\ \mathrm{NH} & \text{—} & \mathrm{CH} \end{array},$$

I.



$$\begin{array}{lcl} \mathrm{NH} & \text{—} & \mathrm{CO} \\ | & & | \\ \mathrm{CO} & & \mathrm{CH} \\ | & & \| \\ \mathrm{NH} & \text{—} & \mathrm{CCH_3} \end{array},$$

II.



$$\begin{array}{lcl} \mathrm{RNH} & & \mathrm{COOC_2H_5} \\ | & & | \\ \mathrm{CO} & & \mathrm{CH} \\ | & & \| \\ \mathrm{NH} & \text{—} & \mathrm{C.CH_3} \end{array}.$$

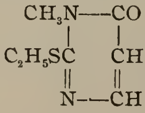
III.

It has been shown in papers from this laboratory[1] that elementary pseudothioureas condense more readily with aldehyde and ketone esters than the normal oxygen ureas. In this paper we describe the behavior of an aliphatic, monosubstituted pseudothiourea towards some ketone esters. We find that they condense to give substituted mercaptopyrimidines, which are easily converted to uracil derivatives by digesting with hydrochloric acid.

Theoretically, 2 isomeric mercaptopyrimidines—1-methyl-2-ethylmercapto-6-oxypyrimidine, V., or 3-methyl-2-ethylmercapto-6-oxypyrimidine, VI., might be formed by condensing ethyl formylacetate with methyl pseudoethylthiourea, IV. We find that they condense to give 1-methyl-2-ethylmercapto-6-oxypyrimidine, V. We obtained no evidence of the formation of the isomeric derivative, VI.:

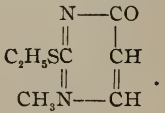
$\mathrm{HN:C(SC_2H_5)NHCH_3}$,

IV.



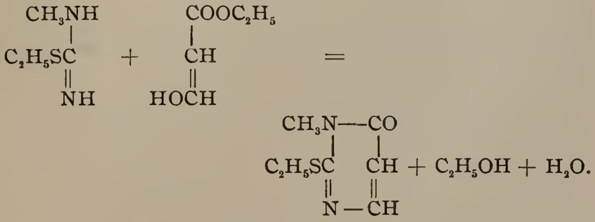
$$\begin{array}{rcl} \mathrm{CH_3N} & \text{—} & \mathrm{CO} \\ | & & | \\ \mathrm{C_2H_5SC} & & \mathrm{CH} \\ \| & & \| \\ \mathrm{N} & \text{—} & \mathrm{CH} \end{array},$$

V.



$$\begin{array}{rcl} \mathrm{N} & \text{—} & \mathrm{CO} \\ \| & & | \\ \mathrm{C_2H_5SC} & & \mathrm{CH} \\ \| & & \| \\ \mathrm{CH_3N} & \text{—} & \mathrm{CH} \end{array}.$$

VI.



$$\begin{array}{r} \mathrm{CH_3NH} \\ | \\ \mathrm{C_2H_5SC} \\ \| \\ \mathrm{NH} \end{array} + \begin{array}{l} \mathrm{COOC_2H_5} \\ | \\ \mathrm{CH} \\ \| \\ \mathrm{HOCH} \end{array} = \begin{array}{rcl} \mathrm{CH_3N} & \text{—} & \mathrm{CO} \\ | & & | \\ \mathrm{C_2H_5SC} & & \mathrm{CH} \\ \| & & \| \\ \mathrm{N} & \text{—} & \mathrm{CH} \end{array} + \mathrm{C_2H_5OH} + \mathrm{H_2O}.$$

V.

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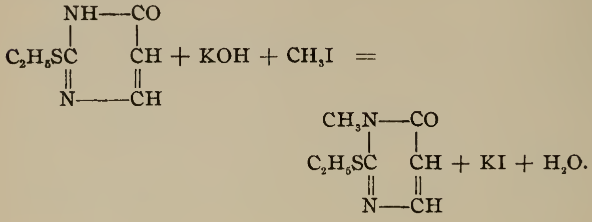
[1] Wheeler and Merriam: This Journal, **29**, 478 (1903). Wheeler and Johnson: *Ibid.*, **31**, 591 (1904). Wheeler and Bristol: *Ibid.*, **33**, 437 (1905).

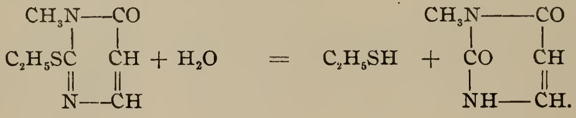
The same mercaptopyrimidine, V., was also obtained when 2-ethylmercapto-6-oxypyrimidine[1] was warmed in alcohol with molecular proportions of potassium hydroxide and methyl iodide.



$$\begin{array}{cc} \mathrm{NH}\!-\!\!\!-\!\!\!- & \mathrm{CO} \\ | & | \\ \mathrm{C_2H_5SC} & \mathrm{CH} \\ \| & \| \\ \mathrm{N}\!-\!\!\!-\!\!\!- & \mathrm{CH} \end{array} + \mathrm{KOH} + \mathrm{CH_3I} = \begin{array}{cc} \mathrm{CH_3N}\!-\!\!\!- & \mathrm{CO} \\ | & | \\ \mathrm{C_2H_5SC} & \mathrm{CH} \\ \| & \| \\ \mathrm{N}\!-\!\!\!- & \mathrm{CH} \end{array} + \mathrm{KI} + \mathrm{H_2O}.$$

V.

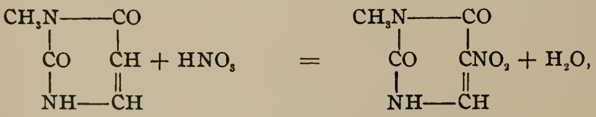
When the mercaptopyrimidine, V., was digested with concentrated hydrochloric acid, it was converted quantitatively into 1-methyluracil, VII., with evolution of ethyl mercaptan.



$$\begin{array}{cc} \mathrm{CH_3N}\!-\!\!\!- & \mathrm{CO} \\ | & | \\ \mathrm{C_2H_5SC} & \mathrm{CH} \\ \| & \| \\ \mathrm{N}\!-\!\!\!- & \mathrm{CH} \end{array} + \mathrm{H_2O} = \mathrm{C_2H_5SH} + \begin{array}{cc} \mathrm{CH_3N}\!-\!\!\!-\!\!\!- & \mathrm{CO} \\ | & | \\ \mathrm{CO} & \mathrm{CH} \\ | & \| \\ \mathrm{NH}\!-\!\!\!- & \mathrm{CH}. \end{array}$$

VII.

The structure of the methyluracil, VII., and the corresponding mercapto derivative, V., was shown in the following manner: It was converted smoothly into 1-methyl-2,6-dioxy-5-nitropyrimidine,[2] VIII., by treatment with fuming nitric and sulphuric acids. Our nitromethyluracil, VIII.,



$$\begin{array}{cc} \mathrm{CH_3N}\!-\!\!\!-\!\!\!- & \mathrm{CO} \\ | & | \\ \mathrm{CO} & \mathrm{CH} \\ | & \| \\ \mathrm{NH}\!-\!\!\!- & \mathrm{CH} \end{array} + \mathrm{HNO_3} = \begin{array}{cc} \mathrm{CH_3N}\!-\!\!\!-\!\!\!- & \mathrm{CO} \\ | & | \\ \mathrm{CO} & \mathrm{CNO_2} \\ | & \| \\ \mathrm{NH}\!-\!\!\!- & \mathrm{CH} \end{array} + \mathrm{H_2O},$$

VIII.

was anhydrous and melted at 264°–265°. The isomeric

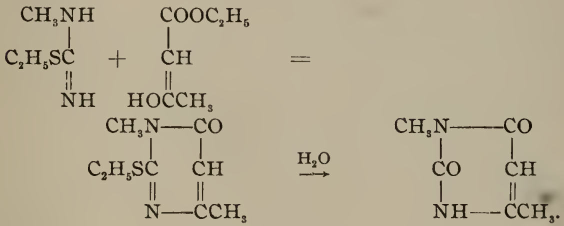
---

[1] Wheeler and Merriam: *Loc. cit.*

[2] Behrend and Thurm: *Loc. cit.*

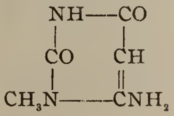
3-methyl-2,6-dioxy-5-nitropyrimidine[1] contains 1 molecule of water of crystallization and melts at 255°–256°.

Methyl pseudoethylthiourea condensed with ethyl acetoacetate to give 1,4-dimethyl-2-ethylmercapto-6-oxypyrimidine, IX. Its structure was confirmed by the fact that it was converted into Behrend's β-dimethyluracil or 1,4-dimethyl-2,6-dioxypyrimidine,[2] X., by treatment with hydrochloric acid.



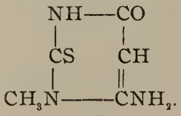
IX. X.

It is interesting to note that methylurea and methylthiourea condense with ethyl cyanacetate to give 2,6-dioxy-3-methyl-4-aminopyrimidine,[3] XI., and 2-thio-3-methyl-4-amino-6-oxypyrimidine,[4] XII., respectively,



XI.

,



XII.

It was shown in a previous paper[5] that pseudoethylthiourea condenses with diethyl formylglycollate to form 2-ethylmercapto-5-ethoxy-6-oxypyrimidine, XIII. We find that ethyl formylphenoxyacetate[6] also condenses with this pseudothiourea to give 2-ethylmercapto-5-phenoxy-6-oxypyrimidine, XIV.:

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[1] Behrend and Thurm : *Loc. cit.*

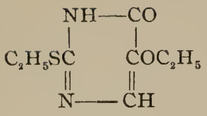
[2] Behrend and Dietrich : *Loc. cit.* Behrend and Thurm : *Loc. cit.*

[3] Conrad : Ann. Chem. (Liebig). **340**, 314.

[4] Trauber and Winter : Archiv Pharm., **244**, 11 (1906).

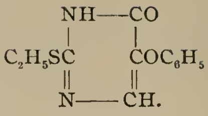
[5] Johnson and McCollum : J. Biolog. Chem., **1**, 437.

[6] Johnson and McCollum : *Loc. cit.*



,

XIII.

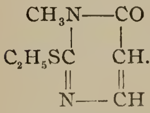


XIV.

EXPERIMENTAL PART.

Methylpseudoethylthiourea Hydriodide, $CH_3NHC(SC_2H_5):NH.HI$, was prepared by treating monomethylthiourea with ethyl iodide. It was obtained as a heavy oil, which finally solidified in a vacuum over sulphuric acid. The salt was extremely hydroscopic and on prolonged exposure to the atmosphere changed to an oil.

1-Methyl-2-ethylmercapto-6-oxypyrimidine,



—Molecular proportions of the above pseudourea hydriodide and the sodium salt of ethyl formylacetate were separately dissolved in the least possible quantities of cold water. The 2 solutions were then combined and treated with an aqueous solution containing 1 molecular proportion of potassium hydroxide. The mixture was allowed to stand at ordinary temperatures for about 12 hours and then heated for a few hours on the steam bath. No crystalline material deposited on cooling. The mercaptopyrimidine was extracted with ether and the ether allowed to evaporate spontaneously, when the pyrimidine deposited in prismatic crystals. They were extremely soluble in hot alcohol and in ether, but soluble with difficulty in cold water. The pyrimidine deposited from alcohol in stout prisms, that melted at 79°–80°, without effervescence, to a clear oil. It was soluble in dilute hydrochloric acid and was precipitated from the acid solution by phosphotungstic acid. Analysis (Kjeldahl):

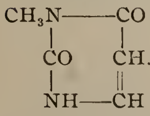
	Calculated for $C_7H_{10}ON_2S$.	Found.
N	16.47	16.6

The same mercaptomethylpyrimidine was also obtained when 2-ethylmercapto-6-oxypyrimidine[1] was treated with methyl iodide under the following conditions: One molecular proportion of potassium hydroxide and 9.8 grams of 2-ethylmercapto-6-oxypyrimidine were dissolved in 50 cc. of 95 per cent alcohol. Twelve grams of methyl iodide were then added and the solution digested on the steam bath until it gave no alkaline reaction with turmeric. It was then cooled, the insoluble potassium iodide separated by filtration and the excess of alcohol removed by evaporation on the steam bath. We obtained a syrup that would not solidify on cooling. After treatment with a small volume of water, to remove any potassium iodide, the mercaptopyrimidine deposited in well-developed prisms. They were crystallized from alcohol and melted at 79°–80°, to a clear oil. When mixed with the above mercaptopyrimidine the melting point was not changed. Analysis (Kjeldahl):

	Calculated for $C_7H_{10}ON_2S$.	Found.	
		I.	II.
N	16.47	16.33	16.6

2-Ethylmercapto-6-oxypyrimidine was recovered unaltered after heating with 1 molecular proportion of methyl iodide for 2 hours, at 155°–165°.

1-Methyl-2,6-dioxypyrimidine (1-Methyluracil),



—One and five-tenths grams of 1-methyl-2-ethylmercapto-6-oxypyrimidine were digested with 15 cc. of 20 per cent hydrochloric acid until the evolution of ethyl mercaptan ceased. When the acid solution was evaporated to dryness the methyluracil deposited in microscopic, prismatic crystals that melted sharply at 174°–175°, without effervescence, to a clear oil. It was extremely soluble in cold water and alcohol but insoluble in benzene. It was not precipitated from its aqueous solution with picric acid. It was dried for analysis at 110° (Kjeldahl):

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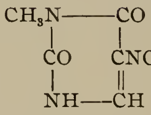
[1] Wheeler and Merriam.

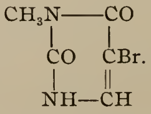
	Calculated for $C_5H_6O_2N_2$.	Found.
N	22.22	22.21

When uracil was heated with 2 molecular proportions of methyl iodide at 186°–200°, for 2 hours, it was recovered unaltered.

	Calculated for $C_4H_4O_2N_2$.	Found.
N	25.0	24.74

1-Methyl-5-nitro-6-oxypyrimidine,[1]  — Four and three-tenths grams of 1-methyluracil were dissolved in a mixture of 15 cc. of fuming nitric acid and 15 cc. of concentrated sulphuric acid, and the solution heated on the steam bath until effervescence practically ceased. The acid solution was then poured upon crushed ice, when a heavy, granular precipitate deposited. The compound was soluble with difficulty in cold water, but deposited from hot water in stout, prismatic crystals that melted at 264°–265°, with effervescence, to a clear oil. It deposited from hot alcohol in hexagonal plates. When the compound was mixed with some nitrouracil the melting point was lowered to 240°. It did not contain water of crystallization. Analysis (Kjeldahl):

	Calculated for $C_6H_5O_4N_3$.	Found.
N	24.56	24.8

1-Methyl-2,6-dioxy-5-brompyrimidine,  — One gram of methyluracil was dissolved in 8 cc. of glacial acetic acid and 1.3 grams of bromine added. Hydrobromic acid was evolved at once and the bromine derivative deposited in prismatic crystals. The compound was soluble in hot water but insoluble in cold. It deposited from 95 per cent alcohol in well-developed, transparent prisms that melted to a clear oil, at 228°–229°. Analysis (Kjeldahl):

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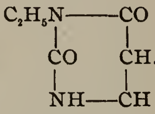
[1] Behrend and Thurm: *Loc. cit.*

	Calculated for $C_5H_5O_2N_2Br$.	Found.
N	13.65	13.68

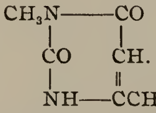
1-Ethyl-2,6-dioxypyrimidine (*1-Ethyluracil*),



—This compound was prepared from 2-ethylmercapto-6-oxypyrimidine as follows: The mercaptopyrimidine was first converted into 1-ethyl-2-ethylmercapto-6-oxypyrimidine by treatment with potassium hydroxide and ethyl iodide, as in the preparation of 1-methyl-2-ethylmercapto-6-oxypyrimidine. The diethylmercaptopyrimidine was obtained as an oil, which, without purification, was digested with concentrated hydrochloric acid until the evolution of ethyl mercaptan ceased. When the hydrochloric acid was removed by evaporation the ethyluracil was obtained as a crystalline deposit. The yield was practically quantitative. It was very soluble in hot water and alcohol. It deposited from benzene in foliated prisms that melted at 173°–174° to a clear oil. Analysis (Kjeldahl):

	Calculated for $C_6H_8O_2N_2$.	Found.
N	20.00	19.75

1,4-Dimethyl-2,6-dioxypyrimidine,



— This compound has been prepared by Behrend and his co-workers.[1] We obtained it by condensing methylpseudoethylthiourea with ethyl acetoacetate to form 1,4-dimethyl-2-ethylmercaptopyrimidine. When this mercaptopyrimidine was boiled with concentrated hydrochloric acid the dimethyluracil was formed with evolution of ethyl mercaptan. It deposited from hot water in prismatic crystals, that melted at 260° to an oil. The compound agreed in its properties with Behrend's 1,4-dimethyluracil. Analysis (Kjeldahl):

---

[1] *Loc. cit.*

	Calculated for $C_6H_8O_2N_2$.	Found.
N	20.00	20.00

Sodium Salt of Ethyl α-Phenoxy-β-oxyacrylate, $NaOCH:C(OC_6H_5)COOC_2H_5$.—Three and two-tenths grams of sodium wire and 1 molecular proportion of absolute alcohol, 6.3 grams, were digested in anhydrous ether until the formation of sodium ethylate was complete. Twenty-five grams of ethyl phenoxyacetate and 10.3 grams of ethyl formate were then added and the ether solution allowed to stand over night, when a colorless, crystalline sodium salt deposited. It was dried in a desiccator over sulphuric acid. Analysis:

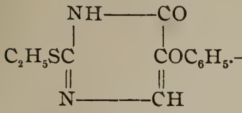
	Calculated for $C_{11}H_{11}O_4Na$.	Found.
Na	10.00	9.65

The free ethyl ester was obtained as a heavy oil when an aqueous solution of the sodium salt was treated with sulphuric acid. It underwent decomposition when we attempted to distil it under diminished pressure.

Hydrazone of Ethyl Formylphenoxyacetate, $C_6H_5NHN:CHCH(OC_6H_5)COOC_2H_5$.—Five grams of ethyl formylphenoxyacetate and 3 grams of phenylhydrazine were warmed together in a water-bath, for 30 minutes. They reacted with evolution of heat to form a yellow, crystalline compound. It deposited from warm, 95 per cent alcohol in yellow prisms, that melted at 219°–221°, with violent effervescence. Analysis (Kjeldahl):

	Calculated for $C_{17}H_{18}O_3N_2$.	Found.
N	9.39	9.3

2-Ethylmercapto-5-phenoxy-6-oxypyrimidine,



—This pyrimidine was formed by condensing pseudoethylthiourea, in aqueous solution, with the sodium salt of ethyl α-phenoxy-β-oxyacrylate. After standing for 6 hours and acidifying with acetic acid, the pyrimidine deposited in prismatic crystals. It crystallized from alcohol in transparent prisms, that melted at 159° to an oil. It responded to a test for sulphur. Analysis (Kjeldahl):

	Calculated for $C_{12}H_{12}O_2N_2S$.	Found.
N	11.29	11.06

New Haven, Conn.,
Feb. 15, 1907.

THE PREPARATION OF POTASSIUM FERRICYANIDE.

By William Jay Karslake.

Two laboratory methods for the preparation of potassium ferricyanide from potassium ferrocyanide seem to be in more or less general use. The one treats the aqueous solution of potassium ferrocyanide with the required amount of either chlorine or bromine, while the other uses a solution of bleaching powder or potassium permanganate, in the presence of hydrochloric acid. At their very best either method gives only fair results and students often fail to get any pure potassium ferricyanide. This difficulty, however, may be overcome by using a dilute aqueous solution of potassium permanganate without the addition of any acid whatever. Somewhat more, about 10 per cent, potassium permanganate is taken than that calculated from the following equation:

$$6K_4Fe(CN)_6.3H_2O + 2KMnO_4 + H_2O = 6K_3Fe(CN)_6 + 2MnO_2 + 8KOH.$$

The method is as follows: To 50 grams of crystallized potassium ferrocyanide, dissolved in 750 cc. of water, is added 7 grams of potassium permanganate, previously dissolved in 250 cc. of water. The mixture is heated on the water bath for about an hour, the precipitated manganese dioxide filtered off, the filtrate evaporated upon the water-bath to crystallization, *i. e.*, to about 150 cc., filtered again if necessary, and allowed to cool. Beautiful, large, red crystals of potassium ferricyanide separate. Yield 25–30 grams, or about 75 per cent of the theory.

University of Iowa,
Feb., 1907.

REPORT.

A Development of the Atomic Theory which Correlates Chemical and Crystalline Structure and Leads to a Demonstration of the Nature of Valency.

Crystallographers have long felt that some fundamental laws must underly the orderly phenomena of crystallography, while chemists have been not less impressed with the belief that the laws governing crystal forms must ultimately throw important light upon the problems of molecular structure. Hitherto, no far-reaching generalizations have been successfully proposed concerning the relations of crystal forms to molecular structure, although many efforts have been made in that direction. Messrs. William Barlow and William Jackson Pope, in a paper bearing the above title, have recently offered such generalizations based upon extended investigations.[1] Their conclusions, if confirmed by further researches, must have far-reaching effects upon chemical and crystallographic conceptions.

Because of the importance of the paper, the review of the article will be preceded by a brief statement of certain earlier views of crystal structure upon which these authors base their work.

Earlier Views of Crystal Structure.

In 1850 Bravais,[2] preceded by Delefosse, proposed a theory of crystal structure which has since been termed the "Raumgitter" theory ("space lattice-work" theory). It is based upon the well-known law that all properties of a crystal are alike in parallel directions. If these properties are dependent upon the nature and arrangement of the crystal molecules, it follows that like crystal molecules have like arrangement in all parallel directions. The structure of crystals thus suggested is illustrated in the accompanying diagram (Fig. I.), where the points represent the centers of gravity of the various molecules, or rather the centers of rest about which the centers of gravity of the molecules may be considered to move. These molecules are discussed as if at rest.

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[1] J. Chem. Soc., 89, 1675 (1906).

[2] Memoire sur les systems formes par des points distribués régulièrement sur un plan ou dans l'espace, Paris: 1850.

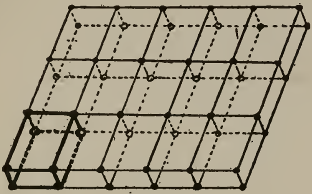

Fig. I.

Fourteen types of arrangement were shown to be possible according to this theory, falling into the 7 well-known crystal systems. As, however, recent work has shown that 32 groups of symmetry exist, it is manifest that the view of Bravais is inadequate to explain all the types of symmetry.

In 1879 Sohncke[1] proposed a further elaboration of the preceding theory. He suggested that several similar "Raumgitters" may be thrust, one into the other, thus producing more complex structures. All possible arrangements were developed by him by the following method. The "Raumgitters" are viewed as first brought into coincidence, and then one displaced from the other by one of three kinds of motion: (1) Translation, in a straight line; (2) rotation of each point of one "Raumgitter" about the corresponding point in the other; (3) a screw motion producing a combination of rotation and translation. In the second case an axis of rotation would exist between each pair of points, while, in the third case, screw axis would develop in similar positions.

Sohncke showed, further, that it is possible in this manner to develop 65 types of arrangement and that they fall into the 32 groups and 7 systems of crystals, in which observation shows that all actually existing crystals are classified. The theory of Sohncke has been further developed by Barlow.[2]

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[1] Entwecklung einer Theorie der Krystalltructur. Leipzig: 1879. *Vide*, Also Sohncke: Z. f. Kryst., 20, 445 (1892).

[2] Z. f. Kryst. u. Min., 23, 1.

Volume and Dimensions of Molecular Space Units.

It can readily be seen, by inspecting Fig. I., that each "Raumgitter" may be viewed as made of units, built up as bricks in a house, to form the completed crystal structure. One of these units is indicated in Fig. I. by heavier lines. Each molecule will be seen to appropriate a space equal to one of these space units, the volume of which is often spoken of as the *molecular volume.* It has been shown that it is possible to calculate the relative volumes of these space units by the following equation:

$$\text{Molecular volume} = \frac{\text{molecular weight.}}{\text{density}}$$

The relative dimensions of the space unit, moreover, may be derived from the measurements of the 3 crystallographic axes, together with a consideration of the physical properties of the crystal, cleavage, etc. Thus, in the general case of a triclinic crystal, illustrated by Fig. II., the 3 edges of the space unit will usually be parallel and proportional to the directions of the 3 crystallographic axes, a, b, c.[1] In this case the following equations hold:

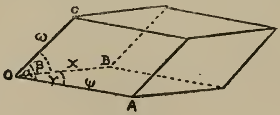

Fig. II.

$$OA : OB : OC = a : b : c,$$

and $COB = \alpha$, $COA = \beta$, $AOB = \gamma$, where α, β, γ, are the angles between the 3 crystallographic axes $c : a$, $c : b$, $a : b$, respectively. Let $OA = x$, $OB = \psi$, $OC = \omega$, then, by a well-known geometrical theorem,

$$V = x\,\psi\,\omega \sin\alpha \sin\beta \sin\gamma \quad \text{whence}$$

$$x = \sqrt[3]{\frac{a^2\,V}{c \sin\alpha \sin\beta \sin\gamma}}$$

$$\psi = \sqrt[3]{\frac{V}{a\,c \sin\alpha \sin\beta \sin\gamma}}$$

$$\omega = \sqrt[3]{\frac{c^2\,V}{a \sin\alpha \sin\beta \sin\gamma}}$$

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[1] *Vide* Groth: Einleitung in die chemisch Kryst., 26.

In this manner the 3 relative dimensions, x, ψ, ω, of the space unit are known. By the use of the above formulae it is possible to investigate the changes in configuration which the molecular space units undergo, when various substitutions occur. The following illustration will make the method clear. Ammonium iodide crystallizes in the isomeric system in cubes, with a cubic cleavage, whence the space unit is cubic. Its molecular weight = 143.83, density = 2.501, whence, molecular volume $= \frac{143.83}{2.501} = 57.51$. Now the 4 hydrogen atoms can be replaced by methyl groups, yielding tetramethylammonium iodide, $N(CH_2)_4I$, which crystallizes in the tetragonal system with a tetragonal cleavage. These salts yield the following data:[1]

	Mol. vol.	x :	ψ :	ω
NH_4I	57.51	3.860	3.860	3.860
$N(CH_3)_4I$	108.70	5.319	5.319	3.842

It will be seen that the value of ω is the same in both cases, while the value of x and ψ have increased in the second compound, showing that the 4 methyl groups have entered the molecule in the plane of the axes a and b (horizontal plane) while the vertical (c) direction, is practically unaffected. In a similar manner, it is possible to investigate the configuration of the space units in various bodies and determine what changes various replacing atoms or groups produce.

The work of Barlow and Pope is based upon the foregoing conceptions concerning crystal structures and molecular configuration. We now proceed to a review of their investigation.

Fundamental Conceptions.

Two fundamental conceptions are presented in the paper:

1. In any chemical body the relative volumes of the atoms are proportional to their valencies. In other words, *valency expresses relative atomic volumes.* Thus, in the molecules of benzene the volume of each carbon atom is 4 times that of each hydrogen atom.

2. In any crystallized body the atoms are "close-packed;" *i. e.*, they are so placed as to occupy the least possible volume.

These conceptions are discussed in 3 aspects: (1) Atomic volume, (2) crystal structure, and (3) the deduced chemical principles.

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[1] Slavek: Z. f. Kryst., 36, 268 (1902). Groth: Einleitung in die Chemische Kryst., p. 32, 1904.

I. Atomic Volumes.

The authors first show that the atomic volume of the same element may vary in different bodies. Thus Tutton, in his work upon alkali sulphates, obtained the following data:

	Mol. vol.	a :	b :	c
K_2SO_4	64.91	0.5727	1	0.7418
Cs_2SO_4	84.58	0.5712	1	0.7531

In substituting caesium for potassium the molecular volume is seen to increase, while the molecular configuration, as shown by the axial ratio, remains unchanged. But since the caesium enters the molecule in a definite position, it seems impossible that the configuration of the molecule should remain constant unless the sulphuric group expands *in the same ratio in which the molecular volume increases*. Hence, the conclusion is drawn that the absolute atomic volume may vary in different chemical bodies though, the ratio of the volume of any constituent to the volume of the molecule may remain constant, as in the case cited. The authors proceed to investigate the relative volumes of the atoms in the same molecule, the absolute volumes not being discussed.

Method of Investigation.

In order to investigate the relation, if any, which may exist between relative volume and valency, the authors reduce all molecular volumes to volumes proportional to the sum of the valencies of the constituent atoms, which they term the "valency volumes." If there is a constant relation between valency and relative volume it should be discovered in this way. The method of procedure is as follows:

Let V = volume of molecule and W = valency volume sought. Dividing the equation

$$V = x \psi \omega \sin \alpha \sin \beta \sin \gamma$$

by V, reduces to unit volume; multiplying the latter by W converts it into the volume W, proportional to the valency. Whence $W = x', \psi', \omega' \sin \alpha, \sin \beta \sin \gamma$. Let $x' = x, \psi' = y$ and $\omega' = z$, then

$$W = xyz \sin \alpha \sin \beta \sin \gamma.$$

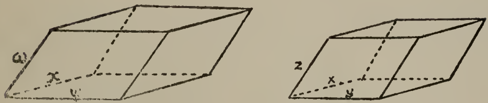
The quantities x, y, z are termed "equivalence parameters." They are the 3 dimensions of the molecular volume when reduced to a volume proportional to the valency W. From the above value of W we obtain the following:

$$x = \sqrt[3]{\frac{a^2\,W}{c \sin \alpha \sin \beta \sin \gamma}}$$

$$y = \sqrt[3]{\frac{W}{ac \sin \alpha \sin \beta \sin \gamma}}$$

$$z = \sqrt[3]{\frac{c^2\,W}{a \sin \alpha \sin \beta \sin \gamma}}.$$

Fig. III. will make the above relations clear.



Volume V, sides x, ψ, ω. Volume W, sides x, y, z.

Fig. III.

Since the lengths of the axes determined by crystallographic measurements express ratios, not different numbers, it is permissible to multiply or divide them. The authors do this rather freely in securing their results, the factors not being entirely free from arbitrary elements.

Using the above method, the authors show that in any molecule *the relative volumes of the atoms are proportional to their valencies.* The evidence adduced is as follows: All cases of substitution may be reduced to 2 types, (1) those in which the sum of the valencies of the substituting and substituted atoms or groups is the same, *e. g.*, in the substitution of hydrogen by chlorine and (2) those in which the sum of their valencies differ, *e. g.*, in the substitution of hydrogen by methyl.

In substitutions of the first types the results show that no change occurs in the configuration of the molecule. This is illustrated by the following data:

	V	W	a	: b	: c	x	: ψ	: ω	: x	: y	z
$CCCl_3$	113.34	14	0.5677	1	0.3160	4.8713	8.5808	2.7115	2.4260	4.2733	1.3503
$CCBr_2Cl$	116.72	14	0.5612	1	0.3171	4.8760	8.6884	2.7551	2.4047	4.2849	1.3587
CBr	120.16	14	0.5646	1	0.3192	4.9647	8.7949	2.7520	2.4090	4.2669	1.3620
$_3CCBr_2$	131.83	14	0.5639	1	0.3142	5.1099	9.0618	2.8472	2.4197	4.2911	1.3483
$_3CCHBr_2$	126.46	14	0.5650	1	0.3118	$\beta = 91°19'$			2.4294	4.2995	1.3406

In the above bodies the values of x, y, z remain essentially constant, showing that, though the absolute volumes of the molecules vary, the configuration of the molecules undergo no change. This indicates that the ratio of the volumes of the substituting and substituted atoms, to the volume of the molecule is constant, otherwise the configuration of the molecule would change. Hence, hydrogen, bromine and chlorine, possessing the same valency, occupy the same relative volume in the molecule, *i. e., their relative volumes are proportional to their valencies.* A number of other bodies were examined and found to conform to the same law.

In cases of the second type, in which the sum of the volumes of the substituting and substituted atoms differ, the relative dimensions of the molecule are found to change, the change in volume being proportional to the change in valency in the bodies studied. Thus in the minerals Chondrodite, Humite and Clinohumite, the following data are obtained:

	W.	a :	b :	c	x :	y :	z	$z/$
Chondrodite, $Mg_3(SiO_4)_2 2Mg(FOH)$	38	1.08630	1	3.14472	2.4249	2.2323	7.0199	0.1
Humite, $Mg_5(SiO_4)_3 2Mg(FOH)$	54	1.08021	1	4.40334	2.4278	2.2475	9.8965	0.1
Clinohumite, $Mg_7(SiO_4)_4 2Mg(FOH)$	70	1.08028	1	5.65883	2.4349	2.2540	12.7547	0.1

These minerals differ by a constant increment, Mg_2SiO_4, having the composition of the Fosterite, which is seen to enter the molecule in the z direction, the x and y values remaining nearly constant. The volume of the molecule is, therefore, proportional to the value of z. But the ratio of z: W is constant, hence the ratio of the volume to the valency is constant, *i. e., the volume is proportional to the valency.* Assuming this principle the authors find it possible to predict the axial ratios $a:b:c$ and the value of $x:y:z$, in the other number of the series, Prolectite and Fosterite, and find that the calculated values approximate to those observed very closely, as shown by the following data:

	W		a :	b :	c	x :	y :	
Prolectite, $Mg(SiO_4)2Mg(FOH)$	22	observed	1.0803	1	1.8862	2.3877	2.2102	4.
		calculated	1.0822	1	1.8500	2.4292	2.2446	4.
Fosterite, Mg_2SiO_4	16	observed	0.9296	1	1.1714	2.4492	2.2769	2.
		calculated	0.9240	1	1.1804	2.4292	2,2446	2.

Two very interesting results are derived from the law thus discussed:

(1) In a number of cases it is shown that water of crystallization causes the expansion of the molecule in one direction, indicating that, in such bodies, the water of crystallization enters the crystal structure in layers.

(2) In the formation of double salts there is usually a simple numerical relation between the valency values of the components, which is shown by the authors to result geometrically from close packing. Thus, in potassium alum,

$$K_2SO_4 \cdot Al_2(SO_4)_3 \cdot 24H_2O,$$

we have the valencies of the parts in the ratio 14:36:96 = 1:3:8.

The general conclusion reached is that, *in any molecule the atoms have volumes proportional to their valencies.*

II. Crystal Structures.

The second principle is that atoms combine in crystals in such a manner as to produce close-packed assemblages. This arrangement springs from the nature of the atoms and the forces uniting them. They are viewed as elastic bodies, acted upon by 2 opposing forces, the attractive forces exerted between them, and the repulsive forces which are designated by the term "elasticity" of the atoms. Under the action of these 2 forces it is held that the atoms would arrange themselves in such a manner as to produce an assemblage occupying the minimum space, *i. e.*, they would be "close-packed."

The principle employed in determining what structure will be assumed by any given number of atoms is, therefore, to ascertain what arrangement will produce close-packing.

In case two or more arrangements are possible, which are nearly equally close-packed, each may occur, thus explaining the phenomenon of polymorphism.

In order to give a mechanical picture, the atoms are represented as elastic spheres which are compressed by the force named, in entering into combinations. In reality, it is assumed that no space exists between them.

In their paper the authors discuss a considerable number of compounds of the aromatic series, promising to publish later results upon extended studies of members of other series which they have already investigated, and which, they state, confirm the conclusions here presented. Their methods may be sufficiently indicated by considering a few of the bodies which they discuss. Of these the most important is benzene, C_6H_6.

Chemical Structure.

The carbon atoms possess a valence of 4 and will have, according to the preceding discussion, 4 times the volume of the hydrogen atoms. Close-packing of such an assemblage will result when the 6 carbon atoms are so placed that each occupies the center of the face of a cube, while the hydrogen atoms occupy the solid angles of the cube. As, however, there are 6 hydrogen atoms and 8 solid angles, it follows that 2 of the angles must be unoccupied. These form the opposite ends of the same diagonal. In the drawings the molecule is so placed that this diagonal is vertical. Fig. IV. shows a model of the benzene molecule, while Fig. V. is a diagram illustrating the arrangement of the atoms in it.

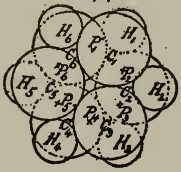


Fig. V.

In assembling these molecules to form the crystal structure, 2 slight distortions are produced which assist in close-packing. In the first distortion the hydrogen atoms are pressed inwards, separating the carbon atoms as illustrated in Fig. VI*a*. In the second distortion the molecules are slightly compressed in one horizontal direction as shown in Fig. VIII.

The molecules are assembled as follows: They are first placed in vertical piles as shown in Fig. VII., the first distortion assisting in this process. These piles are then placed side by side so that alternate tiers, *b–b* in Fig. VIII., stand one-

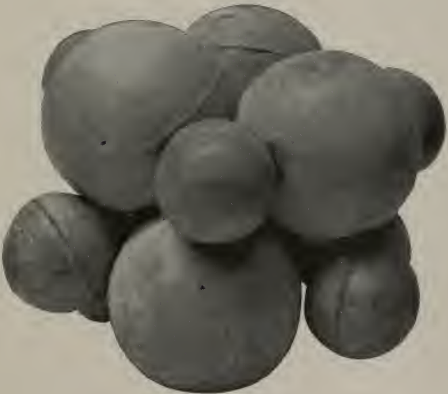


Fig. IV.

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fourth molecule higher than those of the other tiers, *a–a*. In this manner the projecting angles of one pile correspond to the reentrant angles between the adjacent molecules. The second distortion assists in this process. The resulting arrangement is that believed to exist in the benzene crystals. It is illustrated in Fig. VIII., representing one horizontal layer of mole-

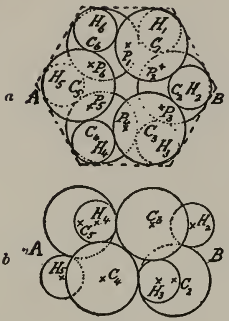

Fig. VI.

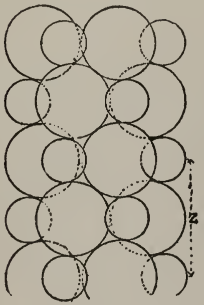

Fig. VII.

cules. In such a structure it is possible to predict not only the system and group in which the substance will crystallize, but its axial ratios as well.

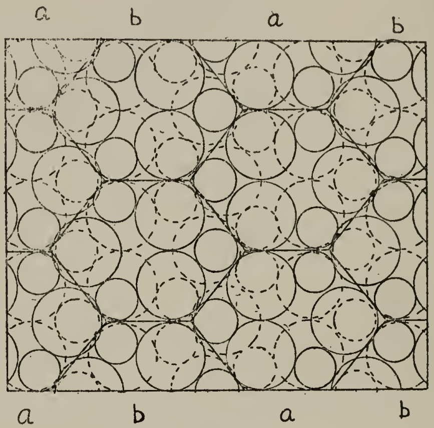

Fig. VIII.

Crystal System.

In Fig. IX. let the intersections of the diagonals represent the centers of gravity of the molecules of Fig. VIII. The diagram then shows the "Raumgitter" as seen in a horizontal plane. The structure represented is seen to possess 3 rectangular directions of symmetry. These consist of the following: (1) Three sets of twofold screw-axes of symmetry, of which 2 lie in the plane of the drawing, indicated by the signs ●—● and ●- - -●, and one perpendicular to it, passing through the centers of the molecules, shown by the signs ●. (2) Three systems of planes of symmetry, 2 perpendicular to the plane of the drawing, shown by the solid lines, and 1 parallel to it. The presence of the latter may be detected by inspecting Fig. VII. Two of these systems of planes are planes of gliding symmetry. All crystals possessing this type of symmetry must belong to the normal group of the orthorhombic system.

Observation shows that benzene actually crystallizes in that system and group.

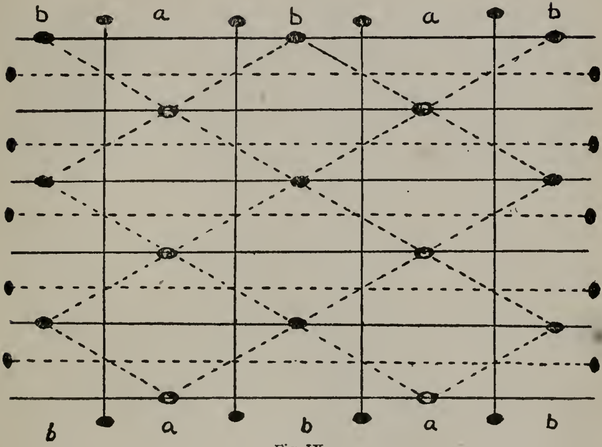

Fig. IX.

Axial Ratio.

The x and y dimensions of the "Raumgitter" unit may be seen by inspecting Fig. X., while the value of z may be observed in Fig. VII. The drawing shows that these possess the values $x = 3.101$, $y = 3.480$, $z = 2.780$, respectively. Inserting these values in the formulae on p. 643, we find $a:b:c = 0.891:1:0.799$. The same values are experimentally obtained by measuring the crystals of benzene. The view pre-

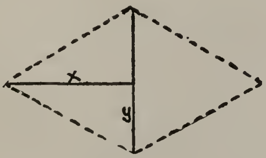

Fig. X.

sented thus receives confirmation from the fact that the crystal symmetry and axial ratios developed theoretically, are identical with those actually observed in the benzene crystals.

Among other bodies studied by the authors are the halogen derivatives of benzene, the dihydroxyl derivatives pyrocatechol, 1,2-$C_6H_4(OH)_2$, resorcinol, 1,3-$C_6H_4(OH)_2$, and hydroquinol, 1,4-$C_6H_4(OH)_2$, triphenylamine, $(C_6H_5)_3N$, triphenylmethane, $(C_6H_5)_3CH$, triphenylbromide $(C_6H_5)_3CBr$, and triphenylacetic acid, $(C_6H_5)_3CCOOH$. Among these, triphenylmethane is of peculiar interest, as showing the manner in which complex molecules may be built up. Fig. XI. shows the authors' conception of the molecules of this substance. All of these bodies are found to give results similar to those already studied.

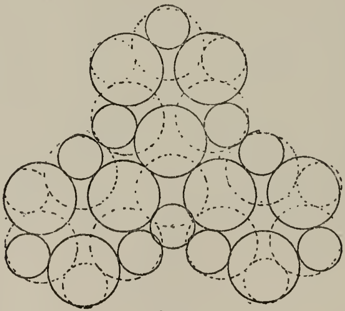

Fig. XI.

The authors also offer a simple explanation of the formation of the multiple benzene rings, naphthalene, Fig. XII., and anthracene, Fig. XIII., and promise a later discussion of their derivatives.

III. Chemical Equivalency.

The authors show that such close-packed assemblages possess 3 geometrical properties which find expression in certain fundamental chemical facts. The latter are: (1) Equivalency; (2) multivalency; (3) partitioning of the molecules.

(1) Equivalency.

In a close-packed assemblage of spheres, single spheres or groups of spheres may be so situated that they can be removed homogeneously, without affecting the arrangement of others. Into the cavities thus formed other spheres of like volume may be inserted, thus reproducing the original arrangement.

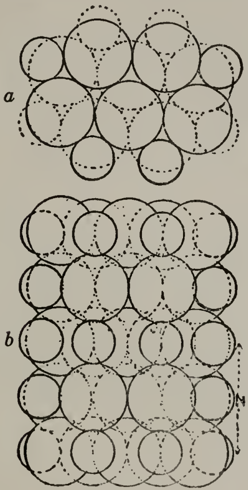

Fig. XII.

This is illustrated by Fig. XIV.

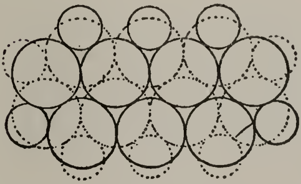

Fig. XIII.

Chemically, this will give rise to equivalency, since atoms can replace others of the same volume in a molecule, without change of structure. Valency itself may be viewed as the expression of the relative volume of atoms. The stability of arrangement of such related substitution products leads to the likeness of crystal form termed *isomorphism*. Hence, both equivalency

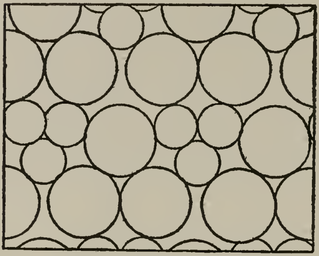

Fig. XIV.

and isomorphism are given a natural explanation by the first geometrical principle.

Certain facts indicate, however, that equivalent atoms, though nearly equal, may differ slightly in volume. Thus Tutton found the following results in his work on the alkali sulphates and selenates:

	V	W	x :	y :	z
K_2SO_4	64.91	12	2.2109	2.1977	2.8463
Rb_2SO_4	73.34	12	2.2049	2.1899	2.8648
Cs_2SO_4	84.58	12	2.2003	2.1826	2.8777
K_2SeO_4	71.67	12	2.2207	2.2083	2.8204
Rb_2SeO_4	79.94	12	2.2147	2.1957	2.8412
Cs_2SeO_4	91.09	12	2.2112	2.1900	2.8524

The differences in the values of x, y, z indicate slight differences in the configurations of the molecule and hence, slight differences in the volumes of the atoms of potassium, caesium and rubidium. The differences are seen to be progressive and indicate that the atomic volumes may change slightly in the same group in the periodic classification, data being given to show that the volume probably increases with increasing atomic weight.

These principles interpret many hitherto unexplained facts, numerous examples being given to illustrate the discussion of the following:

(1) The difference in crystal form of the acids and many of their salts, *e. g.*, sulphuric acid and potassium sulphate. This

fact is explained by the difference in the volumes of the hydrogen and potassium atoms.

(2) The isomorphism of salts of different acids, as in the plagioclase feldspars, $NaAl_2Si_3O_8$ and $CaAl_2Si_2O_8$. Here it is seen that NaSi and CaAl have the same volume and, hence, can replace each other in the molecule.

(3) The isomorphism of elements in complex bodies, though not observed in simple bodies.

(4) The variation observed in crystal form, when replacing atoms have the same valency volume but differ much in form, *e. g.*, in the substitution of nitro, NO_2, by methyl, CH_3.

(2) *Multivalency.*

The second geometrical property may be stated as follows: When like spheres are removed homogeneously from an assemblage and replaced by larger spheres or groups of spheres, the walls of the cavity will be made to gap. Close-packing can only be restored by inserting new spheres in the gap so produced. The authors show that the volume of the latter will be equal to the difference in volume of the replaced and replacing spheres. If V = volume of sphere replaced, then the volume of replacing spheres, to produce close-packing, will equal V, $V + 1 + 1 = V + 2$, $V + 2 + 2 = V + 4$, or $V + n + n = V + 2n$; *i. e.*, the *volume of the replacing atoms differ by intervals of* 2.

Chemically, this principle is expressed by the law of multivalency, that the valencies of an element differ constantly by intervals of 2. Thus, if, in a cavity occupied by an atom of valency m, another atom of the valency 1 be inserted, a second atom of valency 1 is required to fill the gap produced, or if atoms of valency 2, etc., be inserted, additional atoms of the same valency are required to restore close-packing. In other words, the original atom will function as having a valency of m, $m + 2$, $m + 4$, etc., though throughout the operation its volume has not changed. Thus the change of valency by intervals of 2 is fully explained and involves no variation in the actual volume of the atom. In this manner caesium can combine with iodine in CsI, CsI_3, CsI_5, CsI_7, CsI_9, while having a constant volume of 1.

The second geometrical principle is further illustrated in the valencies of radicals. Thus in the replacement of a hydrogen atom by an oxygen atom in ethane, the further addition of an atom of valency 1, such as hydrogen, is required, producing alcohol, C_2H_5OH. Again, in 3 molecules of benzene, H_3 may be substituted by N to produce triphenylamine,

$(C_6H_5)_3N$, but if a carbon atom take the place of H_3 an additional hydrogen atom must be added as is seen in triphenylmethane, $(C_6H_5)_3CH$. The isomorphism of such salts as sodium nitrate, $NaNO_3$, and calcium carbonate, $CaCO_3$, is similarly explained.

(3) *Partitioning of Molecules.*

In the partitioning a close-packed structure of atoms, it may be possible to separate them into molecules in several ways. Various interesting reactions are explained by this principle. This may be illustrated by the formation of the meta-, ortho-, and paradiderivatives of benzene. Let Fig. XV. represent a vertical pile of benzene molecules, the carbon atoms being numbered 1, 2, 3, etc. These atoms can be partitioned into benzene molecules by separation between the planes *ab*, *cd*, etc., or between the planes *bc*, *de*, etc. If replacements occur in the positions 3 and 5, both methods of partitioning will give meta products. If, however, replacements occur in the position a_1, b_4, c_3, d_6, e_5, f_2, etc., the 2 methods of partitioning give, respectively, ortho- and paradiderivatives. Thus may be explained the fact that meta diderivatives are formed alone, while ortho- and paradiderivatives are so frequently produced in the same reaction. The authors

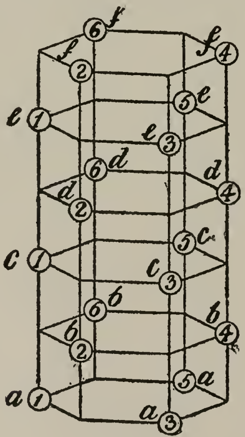

Fig. XV.

promise a later discussion of problems of dissociation based upon this principle.

In conclusion, the authors consider the crystal form of the elements and the relation of the crystalline and amorphous states.

The communication thus summarized is characterized by the wide range of the data discussed, the fruitfulness of its conceptions and the fundamental character of its principles. If correct, these principles must be of universal application and, hence, susceptible of verification at many points. Until they have had such further investigation it would seem proper to withhold judgment, especially in view of the necessary brevity with which the authors have presented their results, and the fact that they have promised further publication in the near future. The character of the work done, the remarkable confirmation offered quantitatively, and the number of facts which it correlates, afford strong presumptive evidence of the correctness of the fundamental conclusions advanced. If the work is so confirmed, the paper will prove to be one of the most important contributions to chemical and crystallographic conceptions which has appeared in recent years.

CHARLES K. SWARTZ.

REVIEWS.

POST'S CHEMISCH-TECHNISCHE ANALYSE. Handbuch der analytischen Untersuchungen zur Beaufsichtigung chemische Betriebe, für Handel und Unterricht. Dritter vermehrter und verbesserter Auflage. Herausgegeben von PROF. DR. BERNHARD NEUMANN. Grossherzoglich technische Hochschule, Darmstadt. Mit zahlreichen eingedruckten Abbildungen. Erster Band. Erster Heft und zweiter Band, Erster Heft. Braunschweig: Friedrich Vieweg und Sohn. 1906. pp. 180 and 208. Price, M. 4.80 and M. 5.50, respectively.

The earliest edition of this work was among the first to bring together, in handy form, the analytical methods employed in the various branches of manufacturing chemistry. In this, and in the second edition, Dr. Post was assisted in the preparation of the material by specialists in different industries. The present edition, although prepared at Dr. Post's suggestion, is brought together by Dr. Neumann without his immediate cooperation, but with the assistance of a considerably larger number of specialists. The plan and general scope of the book remains the same as in the earlier issues, but the entire work has been rewritten and considerably amplified. The editor and his co-laborers have sought to include selected methods and to present the subject matter in concise form. So far as is practicable, the materials involved in each industry are considered under 3 headings: Raw Materials, The Manufacturing Process, and The Finished Product. The work is to be published, as before, in 2 volumes of convenient size, each to include 4 sections, of which the first for each volume is at hand. These sections, each containing the analytical methods relating to certain allied industries, are obtainable in separate form, a rather unusual concession on the part of the publishers.

The subject matter of the first section (Heft) of Volume I. includes the following chapters: Water and Sewage (38 pp.), by Prof. Dr. J. H. Vogel, of Berlin; Fuels (34 pp.), by Dr. H. Langbein, of Niederlössnetz-Dresden; Pyrometrie (36 pp.), and Chimney, Producer and Blast Furnace Gases (72 pp.), both by Dr. B. Neumann, the editor.

The first section of Volume II. treats of the following topics: Lime, Limestones, Cements and Gypsum (80 pp.); Earthenware (92 pp.), and Glass and Glazes (36 pp.), all by Drs. H. Seger and E. Cramer, of Berlin.

The methods given are, naturally, those in use in German laboratories and these differ in some instances from American practice, but this does not seriously lessen the value of the revised volumes. The treatment of the various topics appears to be essentially uniform, although one notices an unfortunate tendency on the part of some of the specialists to omit references to original papers. The text of the previous edition has been but little reproduced in this one, and the whole has been so completely worked over that there has been opportunity to bring the procedures up to date. The revised handbook is well worthy the attention of all practicing chemists, as well as of teachers and students. The remaining sections are promised at an early date and will be awaited with interest.

H. P. TALBOT.

VORTRÄGE ÜBER DIE ENTWICKLUNGSGESCHICHTE DER CHEMIE VON LAVOISIER BIS ZUR GEGENWART. Von A. LADENBURG. Braunschweig: Friedrich Vieweg und Sohn. Pp. 117. 1907. Price, M. 12.

Ladenburg's history is so well known to chemists that it is only necessary to call attention to the fact that it has now appeared in a new edition. The preface is of special interest and may be reproduced advantageously.

The author says: "In issuing the fourth edition of this book, about thirty-eight years after the publication of the first edition, it must be confessed that this is done with a certain feeling of sadness.

"When the first edition appeared in the year 1869 the great chemists Liebig, Wöhler, Bunsen, Kolbe, Kekulé, Dumas, Wurtz, Frankland, Williamson, all of whom I knew personally, and some of whom I could call my teachers, were still living. To-day not only are these dead, but many of my distinguished contemporaries, with some of whom I have worked, as Friedel, Grimaux, Beilstein, V. Meyer, and others, have passed away, and a younger generation, for the most part unknown to me personally, now holds the helm. Hence the feeling of sadness with which I submit this book to the consideration of my colleagues.

"It appears to me meanwhile as though the quiet, certain course of our science has become rapid and tumultuous, and as though the haste and effort that characterizes modern life have also made themselves felt in science. The historian is especially conscious of this condition and it increases his difficulties very greatly in the attempt to gain an objective view and to find the essential that really advances the science. Yet I have believed and considered it to be in accordance with the character of the book that I should follow the development of chemistry down to the present day, and therefore I have added the seventeenth lecture."

This seventeenth lecture has to do with new conceptions of valence, with the calculation of chemical equilibria by means of thermal measurements, solid solutions, allotropy, albumen, catalysis, the chemistry of colloids, etc. I. R.

VAN NOSTRAND'S CHEMICAL ANNUAL, 1907. A Handbook of useful data for Analytical, Manufacturing and Investigating Chemists, and Chemical Students. First Year of Issue. Edited by JOHN C. OLSEN, A.M., Ph.D. With the cooperation of eminent chemists. New York: Van Nostrand Company. 1907. Pp. x + 496. Price, $2.50 net.

The date in the title of this book is apt to prove misleading; the preface was printed November, 1906, a considerable proportion of the contents of the book, so far as they can be identified, refer to 1905 and it is issued in the latter part of March, 1907. The "eminent chemists" referred to are the following: Messrs. A. F. Seeker, E. E. Reid, C. A. F. Kahlbaum, A. Rogers, V. J. Chambers, J. L. R. Morgan, G. P. Pegram and C. H. Lips. The contents of the book consist of the usual tables arranged in the manner customary in works of this class, and containing, as the editor naively remarks, such data as "cannot generally be carried in the mind, but must be readily accessible for use." Considerable experience with them would be necessary in order to form an opinion of their accuracy. The table of the formulae and properties of organic compounds does not make a good impression. Aside from certain peculiarities of selection, which are, perhaps, inevitable, the nomenclature is, in many instances, open to grave objection; to the reviewer the list conveys the impression that it has been made from the German source by one whose familiarity with the subject is limited, and is *not* the familiarity of an organic chemist. Be this as it may, the translation of many of the names of compounds is done very poorly and incorrectly; moreover, they are stated to have been taken from the third edition of Beilstein's "Handbuch," which is, of course, obsolete so far as much of the data required for this "Annual" is concerned. No mention is made of the use of the supplementary volumes of "Beilstein" and, so far as the reviewer has been able to check the data, these volumes do not appear to have been employed. It is hardly possible to believe that this can be the case, but if so, it is entirely inexcusable.

Leaving this point, the question may fairly be asked, "Why use 'Beilstein' at all?" The value of a book such as the one under review lies almost entirely in its data possessing the highest possible degree of accuracy; without this it is worse than useless, and such accuracy can only be obtained by the most careful, laborious collation of the original sources of the facts in question.

A "Review of Chemical Literature" and a list of "New Books," American and English, and of "Foreign Books, mostly German," form the concluding section of the "Annual" and constitute a novelty in compilations of this nature.

The "review" consists of the titles of papers without any other indication of the nature and scope of their contents; obviously, the specialist does not want this kind of thing and it is difficult to understand who else would do so, whereas its omission would have reduced the weight and also, presumably, the price of the volume. The hypothetical purchasers of the "Annual" are, or ought to be members of the American Chemical Society and they, therefore, receive real *reviews* of all important chemical books, annual reports of the progress of chemistry in all its principal branches, with copious references to the literature, and "CHEMICAL ABSTRACTS."

It is a pleasure to praise, without reserve, two features of the volume. The frontispiece consists of an admirable reproduction of a photograph of Sir William Ramsay. The type of the book is clear and the form, paper and binding are attractive. In these respects it is a decided advance on some other chemical works issued by this firm of publishers.

J. BISHOP TINGLE.

A HISTORY OF CHEMISTRY. By F. P. ARMITAGE, M.A., F. C. S., late Exhibitioner of Magdalen College, Oxford. Assistant Master at St. Paul's School. London and New York: Longmans, Green & Co. 1906. Pp. 266. Price, $1.60 net.

Mr. Armitage has written a volume which will be of decided value to students. There was need for a clearly written, brief history of chemistry in English, suited to those who have neither the time nor the knowledge of chemistry requisite for a study of the works of Meyer or Kopp.

This book is well proportioned; it gives little space to the earlier history of chemistry, but from the time of Priestley and Lavoisier is sufficiently full. It concludes with the development of organic and stereo-chemistry, not including modern physical chemistry. Brief sketches of the lives of leading chemists add to the interest of the volume. The author's style is lively and clear. Quotations from the Berzelius-Wöhler letters and from similar sources bring the men, the time and the work near to the reader. Mr. Armitage's history can be warmly recommended to students. E. R.

PRINCIPLES AND PRACTICE OF AGRICULTURAL ANALYSIS, VOL. I. By HARVEY W. WILEY, A.M., Ph.D., Chief Chemist, U. S. Dept. of Agric., Washington, D. C. Easton, Penn.: The Chemical Publishing Co. 1906. Pp. 636. Price, $4.00.

The first volume of this work is devoted exclusively to soils. Part I. deals with the more common minerals, the classification and characteristics of rocks and, finally, with the process involved in the transformation of the latter into soil, the organic constituents of soils being given a brief review. This part would find a more natural place in a work not devoted primarily to a consideration of methods of soil examination, but rather in a distinctive text-book on the origin and properties of soils. Nevertheless, it will serve a valuable purpose for such students as have not previously been taught the elements of mineralogy and geology in their relation to this subject.

Part II. deals very fully and satisfactorily with the entire question of sampling, the importance and value of which in soil investigation cannot be too much emphasized.

In the third part the discussion is not confined to methods, but much of the material presented is of a general character. In this part the author deals with physical properties and with the relations of soils to heat and moisture.

The subject of mechanical soil analysis is treated very fully in the fourth part, descriptions being given in detail not only of the more modern, but also of the earlier methods, in order that the student may familiarize himself with the history of the development of this line of investigation.

Part V. is devoted to the subject of the relations of gases and soils, and deals with questions of absorption, diffusion and methods for the determination of carbon dioxide.

Part VI. begins with a discussion of various miscellaneous determinations such as water, organic matter in its several forms, free organic acids, acidity, etc.; this is followed by a full treatment of the different solvents which have from time to time been recommended for use in soil analysis, and by the various methods for determining the individual mineral constituents which are thereby extracted from soils. Considerable space is likewise devoted to the methods for the determination of nitrogen, amine nitrogen, ammonia, and the volatile nitrogenous compounds of soils. This part closes with a compilation of the soil methods of the Association of Official Agricultural Chemists of the United States.

The subject of nitrification is treated most exhaustively in the seventh part. The discussion deals with the formation of ammonia, the sources of nitrates, the steps involved and the physical and chemical conditions favorable to their formation, the methods and apparatus employed in the study of the nitrifying organisms, methods for determining the nitrifying power of soils and, in fact, with practically every phase of the subject. At the close, the methods for determining nitrous and nitric acid are treated in a full and comprehensive manner.

In the last part the author describes the methods for examining soil waters. Space is also devoted to the special treatment of peat soils and the methods of analysis adapted thereto, and this is followed by a description of the determination of some of the other elements found in certain soils, such for example, as copper, lead, zinc, strontium, boron and titanium.

On the title page of this volume the author speaks of the work as "A Manual for the Study of Soils, Fertilizers, and Agricultural Products, for the Use of Analysts, Teachers and Students of Agricultural Chemistry," from which it will be seen that he did not intend to confine himself to a presentation of mere methods of analysis.

Aside from the first part, the work is far better adapted for advanced students than for beginners, and even the former will use it to best advantage under the direction of an experienced analyst or teacher.

The author has given a critical review of certain methods, but in many instances this has been obviously impossible, much as it might be desired from the standpoint of the inexperienced analyst. This omission is, in some cases, nevertheless, regrettable.

The book seems to be fairly free from typographical and other errors, though a serious mistake is observed at the top of p. 378. The work is a distinctly valuable addition to the agricultural chemical literature and takes rank with the best works of its class in Germany. It will be welcomed with gratitude by all agricultural students and investigators, as well as by specialists in other lines and, owing to the many changes and additions, will be a valuable acquisition even to those who possess the first edition. H. J. WHEELER.

RADIOACTIVE TRANSFORMATIONS. By E. RUTHERFORD, D.Sc. LL.D., F.R.S. MacDonald Professor of Physics, McGill University, Montreal. With Diagrams. New York: Charles Scribner's Sons. 1906. Pp. 287. Price, $3.50 net.

The contents of this book formed the subject matter of a course of 11 lectures delivered by Rutherford, at Yale, in March, 1905, on the Silliman Foundation. The author has selected the more interesting facts and theories in connection with radioactivity and has presented them in a clear and interesting style.

After an introductory lecture, the order of treatment is as follows: Radioactive Changes in Thorium; The Radium Emanation; Transformation of the Active Deposit of Radium; Active Deposit of Radium of Slow Transformation; Origin and Life of Radium; Transformation Products of Uranium and Actinium and the Connection between the Radioelements; The Production of Helium from Radium and the Transformation of Matter; Radioactivity of the Earth and Atmosphere; Properties of the α-Rays; and the Physical View of Radioactive Processes.

While the subject matter is, in general, presented in such form as to be intelligible to those who are not mathematical physicists, yet the treatment is strictly scientific and frequently involves the use of the calculus. This work is, however, much less mathematical than the "Radioactivity" by the same author.

This book is, of course, authoritative, since it comes from one of the leading workers in the field.

It is heartily recommended to all who have a good knowledge of general physics, and an elementary knowledge of the higher mathematics.

Certain mechanical errors in the printing will, doubtless, be removed in subsequent editions. H. C. J.

QUALITATIVE ANALYSIS AS A LABORATORY BASIS FOR THE STUDY OF GENERAL INORGANIC CHEMISTRY. By WILLIAM CONGER MORGAN, Ph.D. (Yale), Assistant Professor of Chemistry in the University of California. New York: Macmillam Co. 1906. Pp. 351. Price, $1.90 net.

The purpose of this book is best explained by quotations from the preface. "This text presents the course of instruction given by the author to the Freshman classes at the University of California where the exigencies of vocational courses render it impracticable for a large number of students to devote more than one year to general inorganic chemistry and to qualitative analysis as well. Therefore, the scheme of qualitative analysis is made to serve as a means of correlating the apparently independent experiments of general chemistry. * * * The course presupposes good chemical training in the secondary schools * * "

"The method of presentation is based principally, though not exclusively, upon the theory of electrolytic dissociation."

The methods used for the separations are the familiar ones. The book seems well suited to its purpose. E. R.

DIE HARZE UND DIE HARZBEHÄLTER MIT EINSCHLUSS DER MILCHSÄFTE. By A. TSCHIRCH. Second Edition. Leipzig: Gebrüder Bornträger. 1906. Two volumes. With 104 illustrations. Pp. xxii + 1268. Price, M. 32.

The appearance, in 1900, of Tschirch's "Die Harze und die Harzbehälter," a well developed volume of some 400 pages, marked a distinct epoch in the literature of this extensive but very vague and unsystematized subject. The second edition of the book shows a remarkable growth to 2 volumes of more than 1200 pages. It is a model of the printer's art, both in type and in illustration. The proof has been carefully read and only an occasional error is noted, such as the substitution of "Shipping" for "Chipping," on page 562. Numerous references to the literature of the subject make the book a most valuable bibliography, and the comfort of the reader is materially increased by the substitution of text figures for the plates at the end of the earlier edition. The omission of the method for Tschugaff's cholesterin reaction, page 1091, is in striking contrast with the completeness of detail which characterizes the book. A feature of the new edition is the compilation, well illustrated, of methods employed in the production and collection of the principal resins. Additional studies of 50 secreta, including the milky juices, such as gutta percha and caoutchouc, help to swell the number of pages. In a praiseworthy spirit of enabling others to repeat, and possibly to correct his work in this difficult field, the author has included details of methods of investigations together with analytical results, the book thereby assuming the character of a laboratory guide.

The fortunate combination of chemist and botanist gives to Prof. Tschirch special qualifications as a leader in such lines of investigation. In the hope of gaining a better foundation for future studies of a more thorough character, his policy in the past has been to broaden rather than to deepen our knowledge of these substances. The difficulties of such work are great, due, primarily, to the fact that so many of the substances are amorphous and without sharp melting points. A distinct service has been rendered, however, by insistence that only specimens of known origin should be studied and that deductions should be based on the behavior of the individual constituents of resins rather than on that of the mixtures from which they are obtained.

The fact that work has only begun in this field is evidenced by the following: The author leaves open the question of the hydroxyl or carboxyl character of resin acids, nor can he decide between $C_{19}H_{28}O_2$ and $C_{20}H_{30}O_2$ as the correct molecular formula for abietic acid. In view of this uncertainty, he holds that any structural formula for the latter is purely conjectural, although many facts point to its being a derivative of an octohydroretene. The relation of ethereal oils to the resins which they accompany is not yet clear, nor can a resin be considered as formed from tannins on the simple evidence that the latter occur near the secretion cells. The author rightly holds that knowledge of the exact chemical character of each class is still too limited to justify such reasoning. In view of such uncertainties it is not a matter of wonder that but little progress has been made in the synthesis of resins.

In the botanical section of the book the views on the seat of resin production and on resin flow are of particular interest. The foundation of this botanical work is the improbability that resins and ethereal oils diffuse through membranes impregnated with water. Several years ago the author demonstrated that the seat of resin production is not in the interior of certain cells from which it is excreted through the membranes of adjacent cells into the intercellular spaces, but lies rather in a well defined, mucilaginous layer, "resinogen Schicht," lining the secretion cells. Numerous subsequent studies have confirmed this view and shown that resins do not wander from cell to cell. The views upon resin flow are of fundamental importance from both scientific and industrial points of view. The author divides resins into two classes. First, "physiological resins," occurring in the normal secretion cells, "primary resin ducts," which form in the plant throughout its growth but yield only a very limited quantity of resin; second, "pathological resins," flowing from "secondary resin ducts," formed in large numbers in the new wood after the infliction of a wound. These secondary ducts are of schizogenous origin and increase in diameter lysigenously. They form an anastomotic system from 5 to 6 cm. in length, opening upon the wound both from above and below. By far the greatest part of the resin flow is from such pathological ducts.

From the fact that secretion cells are formed even in terminal buds, where all available material is needed for forming new wood, and from the further fact that once formed the secreta undergo no further change during the course of vegetation, these secreta are not to be considered as waste products of normal metabolic assimilation, but serve some useful biological end.

All in all, a truly great book is presented to us, a book which will prove itself indispensable to every worker in this field.

CHAS. H. HERTY.

A METHOD OF TEACHING CHEMISTRY IN SCHOOLS. By A. M. HUGHES, B.Sc., Science Mistress of the L. C. C. Secondary School, Eltham, and R. STERN, B.Sc., Science Mistress of the North London Collegiate School. Cambridge: The University Press. 1906. Price, $1.00.

This little book will be found of value not only to teachers of chemistry but also to teachers of nature study in the grades. Educational journals reiterate the words "from the known to the unknown," but few show clearly the practical steps to be taken. The authors of this book, however, have worked out a clear, well-organized plan, starting with common, everyday objects and leading from these into more technical science.

The method of the book is suggestive and for this reason will be helpful even to teachers who do not follow its plan in detail. The authors' idea is to let the teacher take the part of guide, or supervisor, in his classes, allowing the children to create their own problems. Any one using this method will find that he must have a very definite plan for his work, but a plan so elastic that he will find it difficult, if not impossible, to follow closely any book.

Much of the work in the first part of the volume, such as that with limestone, slate, sandstone, etc., might be made more vital to children if used in connection with their geography. The same is true of the simpler experiments on solution and crystallization, which can first be used to advantage in explaining the formations around hot springs and geysers.

The attempt to make the children thoroughly familiar with the chemical characteristics of substances is good, as it secures a sure foundation for more advanced chemistry. One of the chief reasons that chemistry is a difficult subject for many students is due to the fact that the materials used are unfamiliar. It is almost impossible to reason in a science of which the alphabet, so to speak, is unknown. What meaning, for instance, is conveyed to the average mind by the words "sodium hydroxide." The student, however, who has once made the substance out of entirely familiar materials and known its characteristics from childhood, is in a position to use the compound intelligently. The advanced student has no time for these preliminary steps, steps necessary, however, to a thorough knowledge of the science.

The book, with its suggestiveness, can be highly recommended to all teachers of science to children.

M. DRAEGE.

INDEX TO VOL. XXXVII.

AUTHORS.

ACREE, S. F. Formaldehyde color test for proteids............ 604
" On the salts of tautomeric compounds........... 71
" On some semicarbazide derivatives of isopropionic acid, benzoic acid and benzenesulphonic acid.................................... 361
" and *Johnson, J. M.* Studies in catalysis: Rearrangement of acetylhalogenaminobenzene derivatives into halogen acetanilide derivatives.................. 410
Alexeyeff, P. General principles of organic synthesis (Review).. 117
Alway, F. J. and *Gortner, R. A.* Studies on the soils of the northern portion of The Great Plains region: The third steppe....... 1
" and *McDole, G. R.* Studies on the soils from the northern portion of The Great Plains Region: Distribution of carbonates on the second steppe...................... 275
Armitage, F. P. A history of chemistry (Review).............. 659

BAILEY, E. H. S. Text-book of sanitary and applied chemistry (Review).................................. 205
Bevan, E. J. See *Cross, C. F.*
Bingham, E. C. Solubility.................................. 549
Böttger, W. Amerikanisches Hochschulwesen (Review).......... 198
" Principles of quantitative analysis (Review)........ 201
Burrows, G. H. Generation of oxygen from sodium peroxide...... 283

CLASSEN, H. Beet-sugar manufacture (Review).............. 423
Cohen, Ernst. Vorlesungen über anorganische Chemie für Studierende der Medizin (Review)..................... 290
Cram, M. P. See *Tingle, J. Bishop.*
Cross, C. F. and *Bevan, E. J.* Researches on cellulose, II (Review)......................... 199

DENNSTEDT, M. Anleitung zur vereinfachten Elementaranalyse (Review)........................... 289
" Der Nachweis von Schriftfälschungen (Review).................................. 291

Dreaper, W. P. Chemistry and physics of dyeing (Review)....... 420

FERCHLAND, P. and *Rehländer, P.* Monographien über angewandte Elektrochemie (Review).................... 547
Foote, H. W. The double caesium lead bromides............... 124
" and *Levy, L. H.* On the molecular condition of salts dissolved in a fused salt.......... 494
" " " The double ammonium lead chlorides.......................... 119
Fraps, G. S. A simple fat extraction apparatus................ 85
Frazer, J. C. W. See *Morse, H. N.*

GILPIN, J. E. The alkylation of metallic cyanides (Report)..... 543
Gooch, F. A. Outlines of qualitative chemical analysis (Review) 548
Gorsline, E. E. See *Tingle, J. Bishop.*
Gortner, R. A. See *Alway, F. J.*
Grossman, J. The elements of chemical engineering (Review)... 116

HEYL, F. W. See *Johnson, T. B.*
Higley, L. A. On the behavior of sodium and sodium alcoholates towards various esters of acetic acid...... 293
Holland, W. W. See *Morse, H. N.*
Hollard, A. Analyse des métaux par électrolyse (Review)...... 114
Horn, D. W. Determination of transition temperatures......... 619
" On some cuprammonium salts.................... 467
Hughes, A. M. A method of teaching chemistry in schools (Review)..................................... 664

JACKSON, C. L. and *McLaurin, R. D.* On certain derivatives of tetrachlororthobenzoquinone.................. 7
" " " On the constitution of the α- and β-addition compounds of alcohols and tetrabromorthobenzoquinone............. 87
Johns, C. O See *Wheeler, H. L.*
Johnson, J. M. See *Acree, S. F.*
Johnson, T. B. and *Heyl, F. W.* Researches on pyrimidines: Some condensation products of a substituted pseudothiourea: Synthesis of 1-methyluracil........ 628
" See *Wheeler, H. L.*

Jones, H. C. and *Uhler, H. S.* Absorption spectra of certain salts in aqueous solution as affected by the presence of certain other salts with large hydrating power.... 126, 207

" and *Veazey, W. R.* Possible explanation of increase in viscosity when alcohols are mixed with water; negative viscosity coefficients............... 405

KARSLAKE, W. J. Preparation of potassium ferricyanide.... 637

Kohler, E. P. The reaction between unsaturated compounds and organic magnesium compounds........... 369

Kraus, E. H. Essentials of crystallography (Review)........... 422

LADENBURG, A. Vorträge über die Entwickelungsgeschichte der Chemie von Lavoisier bis zur Gegenwart (Review).................................. 656

Levy, L. H. See *Foote, H. W.*

Loevenhart, A. S. Mechanism of carbon assimilation in green plants (Report)........................... 196

Long, J. H. A text-book of elementary analytical chemistry (Review).. 547

Lovelace, B. F. See *Morse, H. N.*

Lucion, R. Monographien über angewandte Elektrochemie (Review).. 204

McDOLE, G. R. See *Alway, F. J.*

McLaurin, R. D. See *Jackson, C. L.*

McLeod, A. F. On aldol, pentaerythrose and the action of copper acetate on the hexoses.................... 20

McPherson, W. Elementary study of chemistry (Review)...... 292

Meade, R. K. Portland cement (Review)...................... 203

Meyer, R. Jahrbuch der Chemie (Review)..................... 291

Morgan, W. O. Qualitative analysis as a basis for the study of general inorganic chemistry (Review)........... 662

Morse, H. N., Frazer, J. C. W. and *Rogers, F. M.* Osmotic pressure of glucose solutions in the vicinity of the freezing point of water....... 558

" " " *Holland, W. W.* The osmotic pressure of cane sugar solutions in the vicinity of the freezing point of water...... 425

Morse, H. N., Frazer, J. C. W. and *Lovelace, B. F.* The osmotic pressure and the depression of freezing points of solutions of glucose..... 324

NEUMANN, BERNHARD. Post's Chemisch-Technische Analyse (Review)........................ 655
Nicloux, M. Contribution a l'étude de la saponification des corps gras (Review)...................... 548

OLSEN, J. C. Van Nostrand's Chemical Annual (Review)...... 657
Ostwald, W. Historical development of chemistry (Review).... 417

PATTISON MUIR, M. M. A history of chemical theories and laws (Review)..................... 544
Pécheux, H. La grande industrie chimique (Review)........... 288

REHLÄNDER, P. See *Ferchland, P.*
Renouf, E. Oxides of the alkali metals (Report)............... 286
" Thiophosphoric acids and thiophosphates (Report). 107
Riley, C. M. Toxicology, the nature, effects and detection of poisons, with the diagnosis and treatment of poisoning (Review).................................. 419
Rogers, F. M. See *Morse, H. N.*
Rutherford E. Radioactive transformations (Review).......... 661

SCHMIDT, ERNST. Aüsfuhrliches Lehrbuch der pharmazeutischen Chemie (Review)................. 419
Smith, G. McP. On reversible metallic displacements in aqueous solutions................................ 506
" *H. C.* Lecture notes on chemistry for dental students (Review).. 202
Stine, O. M. On a method for determining the specific heat of solutions; contribution to the study of hydrates (Report) 112
Swarts, F. Cours de chimie organique (Review)............. 206
Swartz, O. K. Development of the atomic theory which correlates chemical and crystalline structure (Report). 638

TINGLE, J. BISHOP. Glyoxal (Report)...................... 415
" " *Oram, M. P.* Preparation of the aniline derivatives of succinic acid and of phthalic acid......... 596
" and *Gorsline, E. E.* Influence of solvents in the Claisen condensation; catalytic action of ether and tertiary bases in the Claisen condensation and in the Grignard reaction............. 483
" " *Williams, L. F.* Acyl derivatives of *o*- and *p*-aminophenol.............. 51
Tschirch, A. Die Harze und die Harzbehälte mit Einschluss der Milchsäfte (Review)........................... 662
Turner, H. J. Dry method for the generation of oxygen from sodium peroxide............................. 106

UHLER, H. S. See *Jones, H. C.*
VAN LAAR, J. J. Sechs Vorträge über das thermodynamische Potential (Review)....................... 117
Veazey, W. R. See *Jones, H. C.*
WEAVER, E. M. Notes of military explosives (Review)........ 423
Wheeler, H. L., Johnson, T. B. and *Johns, C. O.* Researches on pyrimidines: Synthesis of uracil-5-carboxylic acid.... 392
Wiley, H. W. Principles and practice of agricultural analysis (Review)..................................... 659
Williams, L. F. See *Tingle, J. Bishop.*

SUBJECTS.

ABSORPTION spectra and hydration. *Jones* and *Uhler*........ 126
Absorption spectra of certain salts in aqueous solutions as affected by the presence of certain other salts of large hydrating power. *Jones* and *Uhler*... 126, 207
Acetoacetic benzyl ester, copper salt of. *Higley*................ 310
Acetoacetic ester synthesis. *Higley*.......................... 293
o-Acetoaminophenol, preparation of. *Tingle* and *Williams*..... 57
p-Acetoaminophenol, preparation of. *Tingle* and *Williams*....... 63

Acetylbenzoyl-*p*-aminophenol. *Tingle* and *Williams* 54, 66
Acyl derivatives of *o*- and *p*-aminophenol. *Tingle* and *Williams* 51
Addition compounds of alcohols and tetrabrom-*o*-benzoquinone. *Jackson* and *McLaurin* 87
Aldol, pentaerythrose and the action of copper acetate on hexoses. *McLeod* 20
Alkali metals, oxides of (Report). *Renouf* 286
Alkyl acetates, action of metallic sodium on. *Higley* 316
Alkylation of metallic cyanides (Report). *Gilpin* 543
o- and *p*-aminophenol, acyl derivatives of. *Tingle* and *Williams* 51
o-Aminophenol hydrochloride, preparation and reactions of. *Tingle* and *Williams* 58–61
p-Aminophenol hydrochloride, preparation and reactions of. *Tingle* and *Williams* 66–69
Ammonium lead chlorides. *Foote* and *Levy* 119
Aniline derivatives of succinic and phthalic acids. *Tingle* and *Cram* 596
Aniline dianilinodichlor-*o*-benzoquinone. *Jackson* and *MacLaurin* 16
Apparatus for extraction of fats. *Fraps* 85
Atomic theory and chemical and crystalline structure (Report). *Swartz* 638

BEHAVIOR of sodium and sodium alcoholates towards various esters of acetic acid. *Higley* 293
Benzaldiketohydrindene. *Kohler* 379
Benzaldimethylcyclohexenone. *Kohler* 381
Benzenesulphonic acid, semicarbazide derivatives of. *Acree* 361
Benzoic acid, semicarbazide derivatives of. *Acree* 361
Bromanilic acid. *Jackson* and *MacLaurin* 101

CAESIUM lead bromides. *Foote* 124
Cane sugar solutions, osmotic pressure of. *Morse*, *Frazer* and *Holland* 425
α-Carbethoxysemicarbazido-α-isopropionic nitrile. *Acree* 364
Carbon assimilation in green plants (Report). *Loevenhart* 196
Catalysis. *Acree* and *Johnson* 410
Catalytic action of ether and tertiary bases in the Claisen condensation and the Grignard reaction. *Tingle* and *Gorsline* 483
Chemical and crystalline structure (Report). *Swartz* 638
Claisen condensation, influence of solvents. *Tingle* and *Gorsline* 483
Color test for proteids. *Acree* 604
Constitution of the α- and β-addition compounds of alcohols and tetrabrom-*o*-benzoquinone. *Jackson* and *MacLaurin* 87
Copper acetate, action of, on hexoses. *McLeod* 20
Cuprammonium salts. *Horn* 467

DERIVATIVES of *o*- and *p*-aminophenol. *Tingle* and *Williams* 51
Derivatives of tetrachlor-*o*-benzoquinone. *Jackson* and *MacLaurin*........ 7
Dianilinochlor-*p*-quinoneanil. *Jackson* and *MacLaurin*........ 17
Dianilinodichlor-*o*-benzoquinone. *Jackson* and *MacLaurin*...... 15
Dianilino-*p*-quinoneanil. *Jackson* and *MacLaurin*.............. 18
Dibenzalcyclomethylhexenone. *Kohler*........................ 376
Dibenzoyl-*o*-aminophenol. *Tingle* and *Williams*................ 52, 59
Dimethylcyclohexenone. *Kohler*............................ 381
1,4-Dimethyl-2,6-dioxypyrimidine. *Johnson* and *Heyl*........... 635
Di-*m*- and *p*-nitrobenzoyl-*o*-aminophenol. *Tingle* and *Williams*.. 52, 61
Di-*m*- and *p*-nitrobenzoyl-*p*-aminophenol. *Tingle* and *Williams*........ 55, 56, 68, 69
Diphenylcyclohexenone. *Kohler*............................ 385
Diphenylketocyclohexenone. *Kohler*........................ 386
Diphenylsulphone-*o*-aminophenol. *Tingle* and *Williams*......... 53, 62
Displacements in aqueous solutions. *Smith*.................... 506
Double ammonium lead chlorides. *Foote* and *Levy*............ 119
Double caesium lead bromides. *Foote*........................ 124
Dry method for the generation of oxygen from sodium peroxide. *Turner*........ 106

ETHER, catalytic action of, in the Claisen condensation and the Grignard reaction. *Tingle* and *Gorsline*.................. 483
Ethyl acetanilide and sodium ethylate, action of. *Higley*......... 303
Ethyl acetate and sodium ethylate, action of. *Higley*......... 299
Ethyl alcohol dianilinodichlor-*o*-benzoquinone. *Jackson* and *MacLaurin*........ 16
1-Ethyl-2,6-dioxypyrimidine (1-ethyluracil). *Johnson* and *Heyl*. 635
Ethyldiphenylcyclohexenone. *Kohler*........................ 390
Ethyldiphenylcyclohexenone peroxide. *Kohler*................. 391
Ethyl formylphenoxyacetate, hydrazone of. *Johnson* and *Heyl*.. 636
Ethylidenediphenyltetrahydrobenzene. *Kohler*................ 389, 390
2-Ethylmercapto-5-carbethoxy-6-oxypyrimidine. *Wheeler*, *Johnson* and *Johns*........ 396
2-Ethylmercapto-5-carboxyl-6-oxypyrimidine. *Wheeler*, *Johnson* and *Johns*........ 397
2-Ethylmercapto-5-phenoxy-6-oxypyrimidine. *Johnson* and *Heyl* 637
Ethyl α-phenoxy-β-oxyacrylate, sodium salt of. *Johnson* and *Heyl*........ 636

FAT extraction apparatus. *Fraps*.......................... 85
Formaldehyde color test for proteids. *Acree*.................. 604
Freezing points and osmotic pressure of glucose solutions. *Morse*, *Frazer* and *Lovelace*........ 324

GENERATION of oxygen from sodium peroxide. *Burrows*.... 283
Glucose solution, osmotic pressure and freezing points of. *Morse, Frazer* and *Lovelace*.... 324
Glucose solutions, osmotic pressure of. *Morse, Frazer* and *Rogers*.. 558
Glyoxal (Report). *Tingle*.... 415
Great Plains region, soils of. *Alway* and *Gortner*.... 1
Great Plains region, soils of. *Alway* and *McDole*.... 275
Green plants, carbon assimilation in (Report). *Loevenhart*..... 196
Grignard's reaction applied to unsaturated compounds. *Kohler*. 369
Grignard reaction, influence of solvents. *Tingle* and *Gorsline*... 483

HEXABROM-*o*-QUINONEPYROCATECHIN ether. *Jackson* and *MacLaurin*.... 101
Hexachlor-*o*-dihydroxypyrocatechin ether. *Jackson* and *MacLaurin*.... 13
Hexachlor-*o*-quinopyrocatechin ether. *Jackson* and *MacLaurin* 12, 96
Hexoses, action of copper acetate on. *McLeod*.... 20
Hydrates and specific heats of solutions (Report). *Stine*...... 112
Hydration and absorption. *Jones* and *Uhler*.... 126
p-Hydrazinobenzenesulphonic acid. *Acree*.... 363
o-Hydrazinobenzoic acid. *Acree*.... 365
o-Hydrazinobenzoic acid hydrobromide. *Acree*.... 367
o-Hydrazinobenzoic acid hydrochloride. *Acree*.... 366

INFLUENCE of solvents in the Claisen condensation; catalytic action of ether and tertiary bases in the Claisen condensation and the Grignard reaction. *Tingle* and *Gorsline*.... 483
Isopropionic acid, semicarbazide derivatives of. *Acree*.... 316

MECHANISM of carbon assimilation in green plants (Report) *Loevenhart*.... 196
Metallic displacements in aqueous solutions. *Smith*.... 506
1-Methyl-2,6-dioxy-5-brompyrimidine. *Johnson* and *Heyl*.... 634
1-Methyl-2,6-dioxypyrimidine (1-methyluracil). *Johnson* and *Heyl*.... 633
1-Methyl-2-ethylmercapto-6-oxypyrimidine. *Johnson* and *Heyl* 632
2-Methylmercapto-5-carboxyl-6-oxypyrimidine. *Wheeler, Johnson* and *Johns*.... 405
1-Methyl-5-nitro-6-oxypyrimidine. *Johnson* and *Heyl*.... 634
Methylpseudoethylthiourea hydriodide. *Johnson* and *Heyl*...... 632
1-Methyluracil, synthesis of. *Johnson* and *Heyl*.... 628, 633
Methyl uracil-5-carboxylate. *Wheeler, Johnson* and *Johns* 401
Molecular condition of salts dissolved in a fused salt. *Foote and Levy*.... 494

NATURE of valency (Report). *Swartz*.... 638

m- and *p*-Nitrobenzoyl-*o*-aminophenol. *Tingle* and *Williams*.... 52, 60
m- and *p*-Nitrobenzoyl-*p*-aminophenol. *Tingle* and *Williams*... 55, 67

OBITUARY:
  Bakhuis-Roozeboom, Hendrik Willem.... 415
  Berthelot, Marcellin Pierre Eugène.... 542
  Mendeléeff, Dmitri Ivanowitsh.... 284
  Menschutkin, Nicolai Alexandrowitsch.... 413
  Moissan, Henri.... 413
Octobrom-*o*-quino-1-methoxy-1′-hydroxy-1-monoxide. *Jackson* and *MacLaurin*.... 102
Octobrom-*o*-quino-1-methoxy-1′-hydroxy-1-2,2-trioxide. *Jackson* and *MacLaurin*.... 102
Organic magnesium compounds and unsaturated compounds. *Kohler*.... 369
Osmotic pressure and depression of freezing points of solutions of glucose. *Morse*, *Frazer* and *Lovelace*.... 324
Osmotic pressure of cane sugar solutions in the vicinity of the freezing point of water. *Morse*, *Frazer* and *Holland*.... 425
Osmotic pressure of glucose solutions. *Morse*, *Frazer* and *Rogers* 558
Oxidation of sodium benzylate in dry air. *Higley*.... 307
Oxides of the alkali metals (Report). *Renouf*.... 286
Oxygen from sodium peroxide. *Turner*.... 106

PENTAERYTHROSE, aldol and the action of copper acetate on hexoses. *McLeod*.... 20
Pentachlordiketotetrahydrobenzene. *Jackson* and *MacLaurin*.. 19
β-Phenyl-γ-benzoylbutyric acid. *Kohler*.... 389
β-Phenyl-γ-benzoylbutyric acid, methyl ester of. *Kohler*.... 390
Phenyldimethylcyclohexenol. *Kohler*.... 381
Phenylsulphone-*o*-aminophenol. *Tingle* and *Williams*.... 53, 62
Phenylsulphone-*p*-aminophenol. *Tingle* and *Williams*.... 56, 69
δ-Phenylthiosemicarbazido-α-*o*-benzoic anhydride. *Acree*.... 368
Phthalic and succinic acids, derivatives with aniline. *Tingle* and *Cram*.... 596
Potassium δ-phenylthiosemicarbazido-α-*o*-benzoate. *Acree*.... 368
Proteids, formaldehyde test for. *Acree*.... 604
Pseudothiourea, condensation products of. *Johnson* and *Heyl*.. 628
Pyrimidines. *Johnson* and *Heyl*.... 628

REARRANGEMENT of acetylhalogenamidobenzene derivatives. *Acree* and *Johnson*.... 410
Reports:
  A development of the atomic theory which correlates chemical and crystalline structure. *Swartz*.... 638

Alkylation of metallic cyanides. *Gilpin* 543
Glyoxal. *Tingle* 415
Mechanism of carbon assimilation in green plants. *Loevenhart* 196
Oxides of the alkali metals. *Renouf* 286
Specific heat of solutions; contribution to the study of hydrates. *Stine* 112
Thiophosphoric acids and thiophosphates. *Renouf* 107
Researches on pyrimidines. *Johnson* and *Heyl* 628
Researches on pyrimidines: Synthesis of uracil-5-carboxylic acid. *Wheeler, Johnson* and *Johns* 392
Reversible metallic displacements in aqueous solutions. *Smith*. 506
Reviews:
Amerikanisches Hochschulwesen. *Böttger* 198
Analyse des métaux par électrolyse. *Hollard* 114
Ausführliches Lehrbuch der pharmazeutischen Chemie. *Schmidt* 419
Beet-sugar manufacture. *Classen* 423
Chemical Abstracts (American Chemical Society) 287
Chemistry and physics of dyeing. *Dreaper* 420
Contribution a l'étude de la saponification des corps gras. *Nicloux* 548
Cours de chimie organique. *Swarts* 206
Die Harze und die Harzbehälte mit Einschluss der Milchsäfte. *Tschirch* 662
Elementary study of chemistry. *McPherson* 292
Elements of chemical engineering. *Grossman* 116
Essentials of crystallography. *Kraus* 422
General principles of organic synthesis. *Alexeyeff* 117
Historical development of chemistry. *Ostwald* 417
History of chemical theories and laws. *Pattison Muir* 544
Jahrbuch der Chemie. *Meyer* 291
La grande industrie chimique. *Pécheux* 288
Lecture notes on chemistry for dental students. *Smith* 202
Method of teaching chemistry in schools. *Hughes* 664
Military explosives *Weaver* 423
Monographien über angewandte Elektrochemie. *Ferchland* and *Rehländer* 547
Monographien über angewandte Elektrochemie. *Lucion* ... 204
Nachweis von Schriftfälschungen. *Dennstedt* and *Voigtländer* 291
Outlines of qualitative chemical analysis. *Gooch* 548
Portland cement. *Meade* 203
Post's Chemisch-Technische Analyse. *Neumann* 655
Premier congrès international pour l'étude de la radiologie et de l'ionisation 115

Principles and practice of agricultural analysis. *Wiley*..... 659
Principles of qualitative analysis. *Böttger*.................. 201
Qualitative analysis. *Morgan*.......................... 662
Radioactive transformations. *Rutherford*................. 661
Researches on cellulose. II. *Cross* and *Bevan*.............. 199
Sechs Vorträge über das thermodynamische Potential. *Van Laar*.. 117
Text-book of elementary analytical chemistry. *Long*....... 547
Text-book of sanitary and applied chemistry. *Bailey*...... 205
Toxicology, the nature, effects and detection of poisons. *Riley*.. 419
Van Nostrand's Chemical Annual. *Olsen*.................. 657
Vorlesungen über anorganische Chemie für Studierende der Medizin. *Cohen* and *Romburgh*...................... 290
Vorträge über die Entwickelungsgeschichte der Chemie von Lavoisier bis zur Gegenwart. *Ladenburg*............. 656

SALTS of tautomeric compounds. *Acree*...................... 71
Semicarbazide derivatives of isopropionic acid, benzoic acid and benzenesulphonic acid. *Acree*........................... 361
α-Semicarbazido-*p*-benzenesulphonic acid. *Acree*.............. 363
α-Semicarbazido-*o*-benzoic acid. *Acree*....................... 367
Sodium and sodium alcoholates, behavior of, towards esters of acetic acid. *Higley*.................................. 293
Sodium benzylate and sodium acetoacetic benzyl ester. *Higley*. 313
Sodium benzylate, dissociation of. *Higley*..................... 305
Sodium benzylate, oxidation of. *Higley*...................... 307
Sodium benzylate, reactions with benzyl acetate, ethyl acetanilide and formethylanilide. *Higley*........................... 308
Sodium ethylate and ethyl acetanilide, action of. *Higley*...... 303
Sodium ethylate and ethyl acetate, action of. *Higley*........... 299
Sodium peroxide; a dry method for the generation of oxygen. *Turner*... 106
Soils of The Great Plains region. *Alway* and *Gortner*........... 1
Soils of The Great Plains region. *Alway* and *McDole*........... 275
Solubility. *Bingham*...................................... 549
Solvents, influence of, in the Claisen condensation and the Grignard reaction. *Tingle* and *Gorsline*.......................... 483
Specific heat of solutions; contribution to the study of hydrates (Report). *Stine*.................................... 112
Studies in catalysis: Rearrangement of acetylhalogenaminobenzene derivatives into halogen acetanilide derivatives. *Acree* and *Johnson*... 410
Studies on the Soils of the northern portion of The Great Plains region: The distribution of carbonates on the second steppe. *Alway* and *McDole*.................................. 275

Studies on the soils of the northern portion of The Great Plains region: The third steppe. *Alway* and *Gortner*............ 1
Succinic and phthalic acids, derivatives with aniline. *Tingle* and *Cram*.. 596

TAUTOMERIC compounds, salts of. *Acree*.................. 71
Tertiary bases, catalytic action of, in the Claisen condensation and the Grignard reaction. *Tingle* and *Gorsline*............. 483
Test for proteids. *Acree*.............................. 604
Transition temperatures, determination of. *Horn*........... 619
Tetrabrom-*o*-benzoquinone, addition compounds with alcohols. *Jackson* and *MacLaurin*.............................. 87
Tetrabrom-*o*-quinone. *Jackson* and *MacLaurin*............... 101
Tetrachlor-*o*-benzoquinone. *Jackson* and *MacLaurin*........... 7, 11
Tetraphenyltrimethylcyclohexanone. *Kohler*.................. 378
Thiophosphoric acids and thiophosphates (Report). *Renouf*...... 107
Third steppe: Soils of the Great Plains region. *Alway* and *Gortner*.. 1
Transition temperatures, determination of. *Horn*.............. 619
s-Triphenylbenzene. *Kohler*.............................. 387
Triphenyldihydrobenzene. *Kohler*.......................... 387

UNSATURATED compounds and organic magnesium compounds. *Kohler*... 369
Uracil-5-carboxylic acid. *Wheeler*, *Johnson* and *Johns*......... 399
Uracil-5-carboxylic acid, synthesis of. *Wheeler*, *Johnson* and *Johns* 392
Uracil-5-ethylcarboxylate. *Wheeler*, *Johnson* and *Johns*......... 398
Uracil, formation of. *Wheeler*, *Johnson* and *Johns*.............. 401
Uramidomethylenemalonic ester. *Wheeler*, *Johnson* and *Johns*. 397

VISCOSITY in mixed solvents. *Jones* and *Veazey*............. 405

FORMULAS.

C_4-GROUP.

4 IV.

$C_4H_{11}N_2IS$. Methylpseudoethylthiourea hydriodide. *Johnson* and *Heyl*.. 632

C_5-GROUP.

3 V.

$C_5H_4O_4N_2$. Uracil-5-carboxylic acid. *Wheeler*, *Johnson* and *Johns*.. 399

$C_5H_5O_4N_3$. 1-Methyl-5-nitro-6-oxypyrimidine. *Johnson* and *Heyl* 634
$C_5H_6O_2N_2$. 1-Methyluracil. *Johnson* and *Heyl*................ 633

4 V.

$C_5H_5O_2N_2Br$. 1-Methyl-2,6-dioxy-5-brompyrimidine. *Johnson* and *Heyl*.. 634

C$_6$-GROUP.

3 VI.

$C_6HO_2Cl_5$. Pentachlordiketotetrahydrobenzene. *Jackson* and *MacLaurin*.. 19
$C_6H_6O_4N_2$. Methyl uracil-5-carboxylate. *Wheeler*, *Johnson* and *Johns*.. 401
$C_6H_8O_2N_2$. 1,4-Dimethyl-2,6-dioxypyrimidine. *Johnson* and *Heyl* 635
$C_6H_8O_2N_2$. 1-Ethyl-2,6-dioxypyrimidine (ethyl uracil). *Johnson* and *Heyl*.. 635

4 VI.

$C_6H_6O_3N_2S$. 2-Methylmercapto-5-carboxyl-6-oxypyrimidine. *Wheeler*, *Johnson* and *Johns*.............................. 405
$C_6H_8O_3N_2S$. *p*-Hydrazinobenzenesulphonic acid. *Acree*......... 363

C$_7$-GROUP.

3 VII.

$C_7H_8O_2N_2$. *o*-Hydrazinobenzoic acid. *Acree*.................. 365
$C_7H_8O_4N_2$. Uracil-5-ethylcarboxylate. *Wheeler*, *Johnson* and *Johns*.. 398
$C_7H_{12}O_3N_4$. α-Carbethoxysemicarbazido-α-isopropionic nitrile. *Acree*.. 364

4 VII.

$C_7H_8O_3N_2S$. 2-Ethylmercapto-5-carboxyl-6-oxypyrimidine. *Wheeler*, *Johnson* and *Johns*.............................. 397
$C_7H_9O_2N_2Cl$. *o*-Hydrazinobenzoic acid hydrochloride. *Acree*... 366
$C_7H_9O_2N_2Br$. *o*-Hydrazinobenzoic acid hydrobromide. *Acree*... 367
$C_7H_9O_4N_3S$. α-Semicarbazido-*p*-benzenesulphonic acid. *Acree*... 363

C$_8$-GROUP.

3 VIII.

$C_8H_9O_3N_3$. α-Semicarbazido-*o*-benzoic acid. *Acree*............ 367

C_9-GROUP.

3 IX.

$C_9H_{14}O_5N_2$. Uramidomethylenemalonic ester. *Wheeler, Johnson* and *Johns* 397

4 IX.

$C_9H_{12}O_3N_2S$. 2-Ethylmercapto-5-carbethoxy-6-oxypyrimidine. *Wheeler, Johnson* and *Johns* 396

C_{11}-GROUP.

3 XI.

$C_{11}H_{11}O_4Na$. Sodium salt of ethyl α-phenoxy-β-oxyacrylate. *Johnson* and *Heyl* 636

C_{12}-GROUP.

$C_{12}O_4Cl_6$. Hexachlor-*o*-quinopyrocatechin ether. *Jackson* and *MacLaurin* 12

3 XII.

$C_{12}H_2O_4Cl_6$. Hexachlor-*o*-dihydroxypyrocatechin ether. *Jackson* and *MacLaurin* 13

4 XII.

$C_{12}H_{11}O_3NS$. Phenylsulphone-*o*-aminophenol. *Tingle* and *Williams* 53, 62

$C_{12}H_{11}O_3NS$. Phenylsulphone-*p*-aminophenol. *Tingle* and *Williams* 56, 69

$C_{12}H_{12}O_2N_2S$. 2-Ethylmercapto-5-phenoxy-6-oxypyrimidine. *Johnson* and *Heyl* 637

C_{13}-GROUP.

3 XIII.

$C_{13}H_{10}O_4N_2$. *m*- and *p*-Nitrobenzoyl-*p*-aminophenol. *Tingle* and *Williams* 52, 55, 67

C_{14}-GROUP.

$C_{14}H_{18}O$. Phenyldimethylcyclohexenol. *Kohler* 381

4 XIV.

$C_{14}H_{11}ON_3S$. δ-Phenylthiosemicarbazido-α-*o*-benzoic anhydride. *Acree* 368

5 XIV.

$C_{14}H_{12}O_2N_3SK$. Potassium δ-phenylthiosemicarbazido-α-*o*-benzoate. *Acree* 368

C_{15}-GROUP.

3 XV.

$C_{15}H_{13}O_3N$. Acetylbenzoyl-*p*-aminophenol. *Tingle* and *Williams* 66

C_{17}-GROUP.

$C_{17}H_{16}O_3$. β-Phenyl-γ-benzoylbutyric acid. *Kohler* 389

3 XVII.

$C_{17}H_{18}O_3N_2$. Hydrazone of ethyl formylphenoxyacetate. *Johnson* and *Heyl* 636

C_{18}-GROUP.

$C_{18}H_{16}O$. Diphenylketocyclohexenone. *Kohler* 386

$C_{18}H_{18}O_3$. Methyl ester of β-Phenyl-γ-benzoylbutyric acid. *Kohler* 390

4 XVIII.

$C_{18}H_{12}O_2N_2Cl_2$. Dianilinodichlor-*o*-benzoquinone. *Jackson* and *MacLaurin* 15

$C_{18}H_{15}O_5NS_2$. Diphenylsulphone-*o*-aminophenol. *Tingle* and *Williams* 53, 62

C_{20}-GROUP.

$C_{20}H_{20}$. Ethylidenediphenyltetrahydrobenzene. *Kohler* 389, 390

$C_{20}H_{22}O$. Ethyldiphenylcyclohexanone. *Kohler* 390

$C_{20}H_{22}O_3$. Ethyldiphenylcyclohexenol peroxide. *Kohler* 391

3 XX.

$C_{20}H_{13}O_7N_3$. Di-*m*- and *p*-nitrobenzoyl-*o*-aminophenol. *Tingle* and *Williams* 52, 61

$C_{20}H_{13}O_7N_3$. Di-*m*- and *p*-nitrobenzoyl-*p*-aminophenol. *Tingle* and *Williams* 55, 68, 69

$C_{20}H_{15}O_3N$. Dibenzoyl-*o*-aminophenol. *Tingle* and *Williams*..... 52, 59

4 XX.

$C_{20}H_{18}O_3N_2Cl_2$. Ethyl alcohol dianilinodichlor-*o*-benzoquinone. *Jackson* and *MacLaurin*.................................. 16

C₂₁-GROUP.

$C_{21}H_{22}O_4$. Derivative of benzalacetophenone. *Kohler*........... 386
$C_{21}H_{24}O_2$. Derivative of benzaldimethylcyclohexenone. *Kohler*.. 383

C₂₄-GROUP.

$C_{24}H_{18}$. *s*-Triphenylbenzene. *Kohler*........................ 387
$C_{24}H_{20}$. Triphenyldihydrobenzene. *Kohler*.................... 387

3 XXIV.

$C_{24}H_{19}ON_3$. Dianilino-*p*-quinoneanil. *Jackson* and *MacLaurin*.. 18

4 XXIV.

$C_{24}H_{18}ON_3Cl$. Dianilinochlor-*p*-quinoneanil. *Jackson* and *MacLaurin*.. 17
$C_{24}H_{19}O_2N_3Cl_2$. Aniline dianilinodichlor-*o*-benzoquinone. *Jackson* and *MacLaurin*.................................. 16

C₃₃-GROUP.

$C_{33}H_{32}O$. Tetraphenyltrimethylcyclohexanone. *Kohler*......... 378

ERRATA.

Vol. 35, page 94, line 16, for Tschelnizeff read Tschelinzeff.
" 35, " 94, " *4, for 38 read 37.
" 36, " 612, " 23, for was read were.

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